Y 3.At 7:
37/7-2

REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

ILLINOIS STATE LIBRARY
JUN 8 - 1964

Spring 1964

● VOLUME 7

● NUMBER 2

TECHNICAL PROGRESS REVIEWS

To meet the needs of industry for concise summaries of current atomic developments, the Atomic Energy Commission is publishing this series, Technical Progress Reviews. Issued quarterly, each of the reviews digests and evaluates the latest findings in a specific area of nuclear technology and science.

The five journals published in this series are:

Isotopes and Radiation Technology, P. S. Baker, A. F. Rupp, and associates, Oak Ridge National Laboratory

Nuclear Safety, Wm. B. Cottrell, W. H. Jordan, and associates, Oak Ridge National Laboratory

Power Reactor Technology, W. H. Zinn and J. R. Dietrich, General Nuclear Engineering Corporation

Reactor Fuel Processing, Stephen Lawroski and associates, Chemical Engineering Division, Argonne National Laboratory

Reactor Materials, R. W. Dayton, E. M. Simons, and associates, Battelle Memorial Institute

Each journal may be purchased from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402. *Isotopes and Radiation Technology* at $2.00 per year for subscription or $0.55 for individual issues; the other four journals at $2.50 per year and $0.70 per issue. See back cover for remittance instructions and foreign postage requirements.

The views expressed in this publication do not necessarily represent those of the United States Atomic Energy Commission, its divisions or offices, or of any Commission advisory committee or contractor.

Availability of Reports Cited in This Review

Unclassified AEC reports are available for inspection at AEC depository libraries and are sold by the Office of Technical Services, Department of Commerce, Washington, D. C., 20230. Some of the reports cited are not available owing to their preliminary nature; however, the information contained in them will eventually be made available in formal progress or topical reports.

Unclassified reports issued by other Government agencies or private organizations should be requested from the originator.

Unclassified British and Canadian reports may be inspected at AEC depository libraries. British reports are sold by the British Information Service, 45 Rockefeller Plaza, New York, N. Y.; Canadian reports (AECL series) are sold by the Scientific Document Distribution Office, Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

Classified U. S. and foreign reports identified in this journal as Classified may be purchased by properly cleared Access Permit Holders from the Division of Technical Information Extension, U. S. Atomic Energy Commission, P. O. Box 1001, Oak Ridge, Tenn., 37831. Such reports may be inspected at classified AEC depository libraries.

REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

SPRING 1964

VOLUME 7

NUMBER 2

Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

Contents

Foreword

I COMMERCIAL ASPECTS OF FUEL PROCESSING 83
Fuel-Processing Plans 83
Economics of Fuel Cycles and Chemical Processing 83
References 87

II RESEARCH AND DEVELOPMENT ON AQUEOUS PROCESSING 88
Preparation of Fuel for Processing 88
Solvent-Extraction Separations Processes 89
Chemical Processing in the Transuranic-Element Program 94
Recovery of Neptunium from Solvent Processes 96
Plant and Equipment Design 98
References 102

III RESEARCH AND DEVELOPMENT ON NONAQUEOUS PROCESSING 105
Volatility Processes 105
Pyrometallurgical Processes 113
Other Nonaqueous Processes 121
References 128

IV WASTE DISPOSAL 131
Liquid-Waste Treatment by Ion Exchange and Foam Separation . . . 131
Conversion of High-Level-Activity Wastes to Solids 134
Final Disposal Methods 135
Recovery of Fission Products 141
Corrosion in Waste Processing 143
References 145

V PRODUCTION OF URANIUM, THORIUM, AND PLUTONIUM AND THEIR COMPOUNDS 146
Recovery of Uranium from Ores . . . 146
Production of Uranium Oxides 146
Production of Uranium Carbides and Nitrides 148
Production of Uranium Metal 150
Recovery of Uranium from Refinery Wastes 151
Thorium-Metal Production 154
References 155

(Note: The pagination of this journal will henceforth be consecutive throughout the four issues of each volume.)

Issued quarterly by the U. S. Atomic Energy Commission. Use of funds for printing this publication approved by the Director of the Bureau of the Budget on October 14, 1963.

Section I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

The availability of chemical processing plants and services at the present time is such that the processing of enriched-uranium fuels from European research reactors could be done in either the USAEC's Idaho plant or the British Dounreay plant. The Euratom Community has no processing facilities of its own for high-enrichment fuel.[1]

The total cost of processing European fuels at the Idaho plant must include the high cost of ocean and overland shipment of the spent fuel. This cost must be compared with the total cost of shipment to Dounreay in Scotland plus the United Kingdom Atomic Energy Authority's prices for processing service. These prices have not been announced.

Reduced transportation costs for processing European fuel in the United States could result if AEC opened the Savannah River chemical processing plant to handle high-enrichment fuel from overseas. One of several arguments against this plan is that the jobs are too small to justify an action with so many possible implications.

In 1966 the Nuclear Fuel Services, Inc. (NFS), processing plant is scheduled to begin operations in western New York. Construction of this plant is well under way. Its location will mean that a sizable fraction of the costs of transporting fuel from Europe will be eliminated. The comparative prices for processing high-enrichment fuels at NFS vs. those for processing at Idaho or at Dounreay are still uncertain. However, the AEC will probably not process fuel from Europe at the Idaho plant after the NFS plant is in operation.

Meanwhile, interest is developing in the potential application of a totally different processing technique to high-enrichment fuels. In December 1963, AEC announced that, in response to interest expressed by industry, it was making available certain information relating to fluoride-volatility methods for processing nuclear fuels.[2] The information includes technical data from the AEC chemical processing development program, as well as information concerning the amount of material that would be available as feed for plants using volatility processes.

AEC has been conducting research and development on fluoride volatility for more than 10 years. This processing method employs a different principle from the aqueous processes and depends on converting uranium (and plutonium) to volatile hexafluorides.

The volatility process, until recently, has been directed primarily toward recovery of reactor fuels having a high content of U^{235}. Subject to continued success in the development program, it is believed that volatility technology may in due course be capable of processing civilian power-reactor fuels and thus become an essential part of a competitive private chemical processing industry. Although the economics of volatility technology vs. aqueous technology is as yet undefined, studies in this direction are now under way. As a part of the development, it is possible that some type of demonstration plant program may be undertaken at a future date which might involve significant quantities of fuel from various sources.

Economics of Fuel Cycles and Chemical Processing

Uranium and Plutonium Prices

AEC's five-year contract with Allied Chemical Corp. for the production of refined UF_6 from uranium ore concentrates in the privately owned plant at Metropolis, Ill., expired Mar. 31, 1964. The contract has been renewed on a short-term

basis, i.e., for a period of 90 days. Under the extended contract, AEC will pay a much lower price for the processing service. The new price is reported to be less than half the price under the old contract, which was $1.23 per pound of U_3O_8 processed. Amortization of the plant was to be completed by the end of the five-year contract. AEC is said to be interested in having the plant process recycled uranium from production reactors instead of virgin concentrates in the future. The possibility of doing processing work for private companies, when and if private ownership of reactor fuel becomes a reality, is still uncertain.[3]

AEC has announced that, until Congress passes legislation specifically authorizing it to set a new price for plutonium produced in private reactors, it will pay a price of $10 per gram of Pu^{239} and Pu^{241} as nitrate, with no allowance for other plutonium isotopes.[1] The basis of the price is an AEC estimate of the value of plutonium as fuel for thermal reactors. Presumably, its value as fuel for fast reactors will be considerably higher when such reactors become competitive. The Joint Committee on Atomic Energy (JCAE) has concurred in AEC's plan with the understanding that each proposed purchase will be reviewed by the Committee in advance.

Fuel-Cycle Economics

On Sept. 9–14, 1963, a symposium sponsored by the European Atomic Energy Society on "Fuel Cycles for Nuclear Reactors" was held at Baden-Baden, West Germany. A number of the papers presented at this symposium have become available, several of which are reviewed in the following paragraphs. These papers illustrate a variety of viewpoints on the economic aspects of the nuclear fuel cycle. Opinions vary with the individual, the country, and other circumstances, but there is a certain amount of general agreement discernible in many of the opinions expressed.

Uranium Fuel Cycle in the United States

In a paper by Culler of Oak Ridge National Laboratory (ORNL), the economics of partially enriched fuel cycles and natural-uranium fuel cycles was discussed.[4] This paper points out that much lower fuel-cycle costs than those which exist today are possible with large-cycle capacity. The technology for fuel manufacture and processing now exists, but, because of the small discharge rate of spent fuel and the relatively small requirement for fresh fuel, a coordinated fuel-recycle complex does not exist. Fuel-fabrication plants are small-batch plants which operate far below optimum economic size, frequently on a part-time basis. The one private processing plant (NFS) now under construction is also below optimum economic size.

In spite of these economic handicaps, the emerging nuclear fuel industry in the United States will provide fuel for probably about 1.75 to 2.0 mills/kw(e)-hr for the more advanced stations, such as the proposed Bodega Bay reactor, assuming: (1) private purchase at $13 per kilogram of natural uranium, (2) "toll" enrichment at $30 per kilogram of separative work charge, and (3) a plutonium buy-back price at $8/g, or above.

According to Culler, overall fuel-cycle costs of about 0.8 mill/kw(e)-hr are possible in a single-purpose cycle at a capacity of 10 metric tons of uranium per day for systems fueled with slightly enriched uranium. Much lower fuel-cycle costs are achievable by use of natural-uranium fuels in heavy-water-moderated reactors of very large size. Natural-uranium fuel cycles operated at capacities of 10 tons/day and larger offer overall fuel costs of about 0.05 to 0.18 mill/kw(e)-hr at 28% thermal efficiency. These costs assume 14% per year charge on capital, a 5.5% charge on consumable inventories, burnup of 7000 Mwd/ton of uranium, and a plutonium credit of $6.70/g.

Culler's comparison of the fuel-cycle costs for partially enriched and natural-uranium cycles is given in Table I-1. Because data were taken from a number of sources in preparing this table, there are some internal inconsistencies. (Differences in conversion, fabrication, and shipping charges are probably not as great as shown. Also, if the plutonium credit is based on the current buy-back price of $10/g, the difference is reduced). Culler also points out that the cost of enriching uranium to low enhancement of the U^{235} concentration has not been optimized. It is quite possible that optimized cascades could produce slightly enriched uranium at a lower cost than at present. Nevertheless these uncertainties probably do not change the overall conclusion.

It is apparent from Table I-1 that the fuel-cycle costs for natural uranium and slightly enriched uranium are not greatly different for system capacities of 1 ton/day. However, at 10 tons/day, the overall cycle costs become markedly

Table I-1 COMPARISON OF FUEL-CYCLE COSTS FOR NATURAL AND PARTIALLY ENRICHED FUELS[4]

	Dollars per kilogram of natural U			Dollars per kilogram of partially enriched U	
	1 ton/day	10 tons/day	10 tons throwaway	1 ton/day	10 tons/day
Feed costs	13.00	13.00	13.00	96.17	96.17
Inventory	4.17	3.50	1.43	17.42	17.42
Conversion and fabrication	19.40	7.26	7.26	107.60	37.25
Processing	25.34	3.93	1.00	32.01	6.03
Fuel shipment	1.32	1.27		10.00	10.00
10% contingency	6.32	2.90	2.26		11.45
	69.55	31.86	25.05		
Adjustment*	17.16	3.32	1.48		
Total	86.71	35.18	26.53	263.20	178.59
Put credit at $6.70/g	26.80	26.80		43.30	43.30
	59.91	8.38	26.53	219.90	135.29
Mills/kw(e)-hr†	1.07	0.16	0.51	1.78	1.1
Advanced converter‡					0.8

*Natural-uranium case adjusted to raise capital charge rate from 7.7%/year to 14%.

†For natural-uranium reactor, plutonium yield: 4 g of plutonium per kilogram of uranium at 7000 Mwd/ton. For partially enriched reactor, plutonium yield: 7.5 g of plutonium per kilogram of uranium at 16,550 Mwd/ton.

‡Advanced converter performance expected by 1980.

different and favor the natural-uranium cycle, assuming that Culler's estimates are reasonable. On the basis of the anticipated growth of nuclear power in the United States, an industry that can support a single-unit fuel cycle at a capacity of 10 tons/day may not exist until about 1980.

Uranium Fuel Cycle in Britain

A paper by Allday and Taylor of the United Kingdom Atomic Energy Authority (UKAEA) discussed the economics and other aspects of enriched-uranium fuel cycles in the British nuclear power program.[5] The present British program is based on natural-uranium graphite-moderated CO_2-cooled (Magnox) reactors. By 1970 an Advanced Gas-Cooled Reactor system (AGR), which is fueled with enriched UO_2 pellets clad in stainless steel, is expected to come into operation. In addition to the AGR system, the UKAEA is developing the Steam-Generated Heavy-Water Reactor (SGHW), which is light water cooled and heavy water moderated.

The initial target for fuel life in the AGR system is 12,000 Mwd/ton, but in later AGR's the fuel life is expected to reach 20,000 Mwd/ton. At the latter burnup the reject fuel would contain 5.5 kg of plutonium per ton, but the uranium, containing only 0.35% U^{235}, would have no value. The burning of plutonium in the reactor changes its isotopic constitution as shown in the following table:

	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}
Magnox plutonium	79.0	16.0	4.5	0.5
AGR plutonium, 12,000 Mwd/ton	56.9	30.7	9.7	2.7
AGR plutonium, 20,000 Mwd/ton	45.8	34.7	13.2	6.3

Plutonium-240 and Pu^{242} are nonfissile for thermal neutrons and thus, as irradiation proceeds, the reactivity of this plutonium, in thermal reactors, decreases. If it were not that the thresholds for fission (about 200 kev) of these even-number nuclides lie within the energy spectrum of a fast reactor, a point would be reached at which there would be little incentive to process the fuel. In the long term it is intended to burn this plutonium in fast reactors, and a major part of the British development resources is devoted to this end. In the meantime, utilization of some of the early plutonium in the AGR or SGHW system by substitution for U^{235} is being considered.

Calculated on the basis of a 25-year life, 5% load factor, 3500 Mwd/ton burnup, no plutonium credit, and 6% interest rate, the later Magnox stations are expected to generate electricity at 6 to 7 mills/kw(e)-hr, which includes a fuel-cycle cost of about 1.4 mills/kw(e)-hr.

When enrichment at the current U. S. price scale is used, the estimated AGR costs are 5 to 6 mills/kw(e)-hr, of which the fuel-cycle cost is about 1.6 mills. The corresponding fuel cost for SGHW is expected to be about the same. About two-thirds of the AGR fuel-cycle cost is the cost of enriched uranium [1.1 mills/kw(e)-hr].

Fuel life has a significant effect on fuel-cycle cost, but there is an optimum life which it does not pay to exceed. This is dependent on fuel-fabrication cost, plutonium credit, and fuel rating as well as enrichment costs. For the reference AGR design, the optimum is fairly flat at about 20,000 Mwd/ton.

Table I-2 FUEL-CYCLE COSTS FOR DOR* REFERENCE DESIGN[6]

	Infinite storage		Processing	
	$/kg U	Mills/ kw(e)-hr	$/kg U	Mills/ kw(e)-hr
Fuel-fabrication cost	50.00	0.76	50.00	0.76
Uranium cost	47.07	0.71	47.07	0.71
Transportation cost†	3.00	0.05	21.00	0.32
Processing cost‡			40.20	0.61
Storage cost	4.00	0.06		
Capital charge	10.77	0.16	10.77	0.16
	114.84	1.74	169.04	2.56
Uranium credit			−2.92	−0.04
Plutonium credit§			−27.84	−0.42
Fueling cost	114.84	1.74	138.28	2.10

*Danish organic reactor.
†Includes transportation cost for new fuel and spent fuel.
‡Includes cost of converting uranium to UF_6.
§Based on $10 per gram of contained Pu^{239} and Pu^{241}.

Uranium Fuel Cycle in Denmark

The fuel-cycle economics for a heavy-water-moderated organic-cooled reactor concept in Denmark was discussed by Olgaard of the Danish Atomic Energy Commission.[6] Fueling costs were calculated for two cases, one involving infinite storage of the spent fuel and the other involving chemical processing. Costs were based on AEC charges for initial uranium and for processing. The spent-fuel batch size was between 2 and 8 tons of uranium so that the "turnaround" time for the processing plant was equal to the processing time. After the uranium was processed, it was converted into UF_6 at a price of $5.60 per kilogram of uranium while the plutonium remained in the form of nitrate. The cost of infinite storage of the fuel was taken as $4 per kilogram of uranium, including transportation to the storage site.

For all cases considered the fueling cost was lower for the infinite storage approach than for chemical processing, as illustrated in the example shown in Table I-2 for fuel consisting of UO_2 enriched to 1% U^{235}.

In Table I-2 the uranium credit is less than the $5.60/kg charge for converting uranyl nitrate to UF_6. In such a situation the uranium would probably be converted to oxide and stored at a net saving of about $2 per kilogram of uranium over the costs shown in the table. [However, it might be questioned whether the AEC charge of $5.60/kg for the chemical conversion to UF_6 is realistic for depleted uranium in view of the low cost for similar service performed by Allied Chemical Corp. (see above). It should also be noted that the fuel-processing cost is high for this case because of the small load and the high percentage of turnaround time. The spent-fuel transportation cost is also high because of the assumption that the fuel would be shipped to a U. S. processing facility.]

Olgaard states that chemical processing will ultimately be profitable because the price of uranium and plutonium will increase, whereas the cost of processing will decrease with bigger processing plants. However, the author does not believe that this situation will arise in the next 20 years.

Plutonium Utilization in Fuel Cycles

The utilization of plutonium in fast and thermal reactors was discussed in a paper by Eschbach of Hanford Laboratories.[7] The author states that the following general principles and technology of plutonium refueling are commonly acknowledged:

1. Plutonium has a clear superiority over other fuels in fast reactors.
2. Plutonium is a valuable fuel for thermal reactors.
3. The special handling occasioned by plutonium's toxicity will involve nominal, if not negligible, costs when plutonium is utilized in significant quantities.
4. Plutonium-240 imparts unique functions to plutonium fuels in thermal reactors because of

its potential for simplifying thermal reactor control.

In contrast to the foregoing, the methods to be used, the resulting economics, and the timing of events associated with plutonium utilization are not subjects of such general accord as those above. Studies do, however, indicate that plutonium fuels can be used in a wide variety of ways. The fueling systems that have been considered embrace the range from minor spiking with plutonium to complete reactor loads with plutonium intimately mixed in the fuel for a variety of fuel management schemes and virtually every reactor type. Fuel loads comprised of U^{238} and thorium enriched with appropriate mixtures of plutonium, U^{233}, and U^{235} can also be considered. Further complication is afforded by considering exchange of fuels between fast and thermal reactors. With all this in mind, it is noteworthy that, for some time, the major utilization of plutonium will be *in situ*, especially in slightly enriched uranium fuels.

The subject of plutonium utilization in Great Britain was discussed in a paper by Kronberger.[8] Power stations in Britain will produce large quantities of plutonium. The buildup of plutonium stocks is expected to reach 25 metric tons by 1976 and 45 metric tons by 1980, unless this material is utilized. The 25 tons of plutonium could, in the form of fast-reactor fuel elements (as the initial charge), be capable of producing power of nearly 10,000 Mw(e).

Economic assessments have been made of the value of plutonium to individual reactor systems. However, a more logical approach, according to this author, is to consider plutonium as an intermediate product in an integrated system of plutonium-producing and plutonium-bearing reactors, in which case there is no need to assign a value to plutonium, the aim being to devise an optimum combination of reactors to provide a minimum overall generating cost. This approach is now under development in the UKAEA, and the method is described in another British paper by Iliffe.[9]

An evaluation of the economics of plutonium as a fuel in heavy-water reactors of the type under development in Sweden is presented in a paper by Zettergen.[10] Some of his conclusions are:

1. The potential value of plutonium, with costs assumed to be prevailing in the late 1970's, is estimated to be $8 to $15 per gram of fissile plutonium, depending on reactor type.

2. With costs estimated for the early 1970's, plutonium can probably not compete with U^{235} enrichment. The present Swedish fuel policy calls for stockpiling of the spent fuel. Plutonium recycle offers a potential alternative, however, should the price or availability of enriched uranium develop unfavorably or the processing and plutonium fuel-fabrication costs develop unfavorably.

3. The heavy-water reactors considered make efficient *in situ* use of plutonium and are much less dependent on the receipt of plutonium credit than reactors with poor neutron economy, for which processing is a necessity. (A. A. Jonke)

References

1. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 10(11): (November 1963).
2. AEC Responds to Industrial Interest in Fluoride Volatility Processing, AEC Press Release IN-467, Dec. 11, 1963.
3. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 10(10): (October 1963).
4. Floyd L. Culler, Jr., Partially Enriched Fuel Cycles, USAEC Report ORNL-TM-678, Oak Ridge National Laboratory, September 1963.
5. C. Allday and H. A. Taylor, Enriched Uranium Fuel Cycles, Paper presented at the European Atomic Energy Society's Symposium on Fuel Cycles for Nuclear Reactors at Baden-Baden, Germany, September 9–14, 1963.
6. P. L. Olgaard, Fuel Cycle Investigations for a DOR Type Reactor, Paper presented at the European Atomic Energy Society's Symposium on Fuel Cycles for Nuclear Reactors at Baden-Baden, Germany, September 9–14, 1963.
7. E. A. Eschbach, Utilization of Plutonium in Fast and Thermal Reactors, Paper presented at the European Atomic Energy Society's Symposium on Fuel Cycles for Nuclear Reactors at Baden-Baden, Germany, September 9–14, 1963.
8. H. Kronberger, Utilization of Plutonium and Plutonium Fuel Cycles, Paper presented at the European Atomic Energy Society's Symposium on Fuel Cycles for Nuclear Reactors at Baden-Baden, Germany, September 9–14, 1963.
9. C. E. Iliffe, Economics of Plutonium Utilization in Programs of Nuclear Power, Paper presented at the European Atomic Energy Society's Symposium on Fuel Cycles for Nuclear Reactors at Baden-Baden, Germany, September 9–14, 1963.
10. L. Zettergen, Plutonium as a Fuel for Heavy Water Reactors, Paper presented at the European Atomic Energy Society's Symposium on Fuel Cycles for Nuclear Reactors at Baden-Baden, Germany, September 9–14, 1963.

Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

The recovery of fertile and fissionable materials from spent nuclear fuels continues to be accomplished principally by solvent extraction of aqueous solutions of fuel materials. Process and equipment research and development activities emphasize methods for preparing fuel elements for such treatment and the utilization of a greater variety of solvents. There is considerable work under way on the solvent-extraction separations of transuranium elements and on the recovery of neptunium in fuel-processing operations for the production of Pu^{238}.

Preparation of Fuel for Processing

There appears to have been no recent work of significance on mechanical fuel preparation methods. The principal work of interest concerns the treatment of zirconium-clad and matrix fuels by chlorination or hydrofluoric acid to prepare solutions for solvent extraction.

Dissolution of Zirconium Alloy in Dilute Hydrofluoric Acid

Work has continued at the Idaho Chemical Processing Plant (ICPP) on the improvement of the hydrofluoric acid process for the dissolution of zirconium-uranium alloy reactor fuels. It was previously noted[1] that the use of dilute (5*M*) hydrofluoric acid, rather than more concentrated (10*M*) hydrofluoric acid (used in the process previously operated at the ICPP), as the dissolving reagent offered advantages over the previous process as follows: (1) the complete dissolution of alloy of higher uranium content (about 2% uranium vs. less than 1% uranium possible in the previous process) and (2) the avoidance of strong and corrosive oxidizing agents. A continuous dissolution process, with its attendant potential economies in labor and equipment capacity, also appeared to be possible. In recent work,[2] Newby at the ICPP has found that operation at temperatures well below the boiling point permits still more uranium to be retained in the solution. In small-scale tests, all the zirconium and uranium, and one-third of the tin, in a 2.5% uranium–Zircaloy-2 alloy could be dissolved continuously and retained in solution with 5*M* hydrofluoric acid at dissolution temperatures of 60 to 80°C and a dissolver reagent feed rate-to-fuel surface ratio of 0.04 $cm^3/(min)(cm^2)$. A clad alloy composition containing overall about 2.2% uranium is about typical of what is expected in the process.

In experiments with 3% uranium fuels, difficulty was experienced with the buildup of uranium-containing solids in the dissolver. This effect was essentially eliminated by operation at 60°C and by recirculation of the dissolvent, or by other solution motion which would tend to prevent deposition of suspended uranium tetrafluoride on the walls of the tall pipe dissolver. It appeared possible to retain slightly more uranium in solution with downflow than with upflow operation of the dissolver.

In batch dissolution, oxidizing agents such as chromate or peroxide can be used to convert part of the uranium present to the six-valent state and thus permit more to be retained in solution. In continuous dissolution, however, the simultaneous production of hydrogen suggests difficulty in maintaining oxidizing conditions for uranium. In dissolution tests with 3% uranium alloy and 4.8*M* hydrofluoric acid, the oxidizing agents, nitric acid, chromic acid, aluminum nitrate, and hydrogen peroxide were investigated at concentrations ranging from 0.03*M* to 0.5*M*. The rate of corrosion of a Monel coupon in the

dissolver was also determined. In no case was all of the uranium retained in solution, although the amount undissolved was reduced to 1 or 2%, and dissolution rates were decreased. Corrosion of Monel was increased significantly by the presence of oxidizing agents.

Hydrofluoric Acid Treatment of Zirconia-Urania Mixtures

In other work at the ICPP, the dissolution of an advanced pressurized-water reactor (PWR) fuel, composed of ceramic pellets of mixed zirconium and uranium oxides clad in Zircaloy, is being investigated.[3] The cladding, of course, may be dissolved readily in hydrofluoric acid, but the oxides are quite refractory. Reagents composed of concentrated hydrofluoric acid, with small amounts of nitric, boric, and oxalic acids, appear promising, although dissolution rates are slow. Cladding was removed with 4 *M* or 5 *M* hydrofluoric acid at 70°C with a uranium loss of only 0.5%. The core material was then dissolved in 16 *M* hydrofluoric acid containing 0.03 *M* nitric acid, 0.37 *M* boric acid, and 0.05 *M* to 0.5 *M* oxalic acid. Oxalic acid does not appear to affect the initial dissolution rate but decreases the time necessary for complete dissolution and increases uranium solubility.

Preparation of Zirconium-Alloy Fuel by High-Temperature Chlorination

At Oak Ridge, considerable development work has been done on a method (the Zircex process) for treating zirconium-enriched uranium-alloy fuels by high-temperature hydrochlorination in order to separate the zirconium from the uranium as the volatile tetrachloride. A good description of the process appeared previously.[4]

Gens has recently described[5] a proposed modification of this technique in which both uranium and zirconium are volatilized by treatment with chlorine, and the chlorides are then absorbed in water for separation by solvent extraction. It was shown that zirconium tetrachloride could be absorbed efficiently by passing the chlorination vapors into the vapor space of a vessel containing boiling water to form highly soluble zirconyl chloride and hydrochloric acid. A small amount of insoluble zirconium oxide is formed in this step by further hydrolysis. The mixed chlorides in solution may be separated directly by solvent extraction with tributyl phosphate (TBP) with the addition of a small amount of nitric acid, or the bulk of the chloride may be removed by treatment with hydrogen peroxide, to yield chlorine for recycle, according to the following reaction:

$$2HCl + H_2O_2 \rightarrow Cl_2(g) + 2H_2O$$

Some of the hydrogen chloride present also volatilizes and passes off with the chlorine. About 75% of the initial chloride was readily removed from solutions 4 *M* in zirconium and 12 *M* in chloride by treatment with 50% of the amount of peroxide stoichiometrically equivalent to the chloride, with simultaneous concentration of the solution to 6 *M* to 7 *M* zirconium.

Solvent-Extraction Separations Processes

The process chemistry of plutonium in solvent extraction has been further investigated, and methods for transuranium-element processing have been reported in detail. Some work on new solvents is continuing. Additional papers from the Gatlinburg Solvent Extraction Chemistry Symposium, which were previously reviewed, have been published.[6–8] The last of these articles,[8] on the EUREX process, is further discussed in this issue.

Tetravalent Uranium as the Plutonium Reductant in TBP Processing

In the Purex (TBP extraction) process, separation of uranium from plutonium is accomplished after extraction into the solvent by reducing plutonium to the trivalent state, which strongly favors the aqueous phase. Ferrous sulfamate or its equivalent in other compounds is most used for this purpose but is disadvantageous in that it contributes iron salts and sulfate ions to the outflowing streams. Consequently it has been proposed that ferrous sulfamate be replaced by tetravalent uranium, stabilized by hydrazine, as its nitrate salt. This would contribute no undesirable ions to the waste or other process streams. A report of work on this process modification in the United Kingdom (U. K.), in which uranium is reduced electrolytically, has previously been given,[9] and other work has been carried out at the Savannah River and Hanford Laboratories. The U. K.

work showed that the uranium reductant solutions were stable for several weeks and should be usable for plutonium partition in a mixer-settler extractor under conditions planned for the new fuel-processing plant at Windscale.

Further work has been published recently by McKay, Streeton, and Wain[10] on laboratory-scale mixer-settler tests of hydrazine-stabilized U(IV) reductant to develop optimum conditions for plutonium partition and to confirm process feasibility. The results of 13 mixer-settler runs, four with plutonium present, under typical flow-sheet conditions using 30% TBP in hydrogenated propylene tetramer are reported. The conclusions of these authors are as follows:

1. The aqueous-phase acidity should not fall below about 0.5*M* at any point in the contactor, to avoid losses of U(IV) by air oxidation.
2. The aqueous acidity in the section in which the aqueous phase is contacted with fresh TBP-diluent mixture should be between 2.5*M* and 3*M*. Higher acidities would lead to plutonium oxidation and recycling, whereas lower acidities would lead to inadequate removal of tetravalent uranium from the aqueous stream.
3. The feed concentration of tetravalent uranium need not exceed four times that required stoichiometrically for plutonium reduction. Only a small concentration (~0.01*M*) of hydrazine is needed as a stabilizer to keep the system free of nitrous acid. Reduction of Pu(IV) by U(IV) occurs rapidly in both the organic and aqueous phases.

Some work was carried out on other amino compounds as alternates for hydrazine by adding nitrous acid to their mixtures with ferrous iron [used as a stand-in for Pu(III)]. Immediate oxidation of iron was noted with urea, formamide, acetamide, and methylamine, whereas no oxidation of iron was noted with sulfamic acid or hydrazine until all the stabilizer of iron was used up. As sulfamic acid introduces sulfate to the system, only hydrazine among this group of compounds appeared to be suitable.

The EUREX Process for Uranium-Aluminum Alloy (Amine Extraction)

Further details have been published[8] on the EUREX process for processing uranium-aluminum alloy with a tertiary amine solvent, a report of which was given at the Gatlinburg Solvent Extraction Chemistry Symposium.[11] It is intended to construct a small plant in Italy using this process to recover enriched uranium from Materials Testing Reactor (MTR) type fuel assemblies. Expected advantages of the process result from the higher selectivity of the amine solvent which may permit a high decontamination factor and a reduction in the number of extraction cycles, as compared to hexone or TBP processes. Good stability of the solvent toward radiation and other deteriorating effects is observed.

As with other enriched uranium-aluminum alloy extraction processes (hexone-25, TBP-25), the first cycle is based on using the salting strength of the concentrated aluminum nitrate solution (1.7*M*), produced by nitric acid dissolution of the alloy, to obtain high organic-aqueous distribution coefficients for uranium in contact with the solvent. The latter is composed of 4 vol.% of tricaprylamine (TCA or Alamine 336, which also contains some related tertiary amines) in an aromatic hydrocarbon diluent. The aluminum nitrate-scrubbed product stream is stripped into one-fifth the feed volume of acidified water and passes without concentration (at a uranium content of 9.6 g/liter) to a similar second cycle for further decontamination by the same solvent. Plutonium is partitioned to the second-cycle raffinate. The chemical flow sheet is shown in Fig. II-1.

With dilute tertiary amine solvent, sufficient extraction power is not obtainable for a practical process if nitric acid is the only salting agent. As the acid concentration is increased to 6*M*, the uranium distribution coefficient rises to a peak value of a few tenths and then falls off rapdily. With metal nitrate salting agents, and particularly with aluminum nitrate, the distribution coefficients at equivalent nitrate concentration above 2*M* are almost an order of magnitude greater, presumably due to the formation of trinitratouranyl ion, and satisfactory extraction power is obtained.

The selection of the optimum concentration of amine in the diluent was based on a compromise between extraction coefficient and beta-gamma decontamination factors. As shown in Fig. II-2, for an aqueous-phase composition similar to that of the flow-sheet feed composition, the uranium distribution coefficient increases almost linearly from 1 to 7 as the amine concentration is increased from 2 to 10%. Over the same range, beta and gamma decontamination factors drop sharply from 800 to 1500 to the order of 110, leveling off somewhat

in the vicinity of 5% amine. Good decontamination therefore appears to require a fairly low amine concentration.

Stage requirements for the six contactors in the process, to maintain uranium losses not exceeding 0.5 mg/liter in exit streams (or a total of 0.15% of the feed), are not large, varying from 4 to 7.2 theoretical stages. The largest requirement is for 7.2 stages in the second-cycle extractor.

The decontamination performance of the process over two cycles has been studied by batch equilibration techniques at levels up to about 5% of that expected. As shown in Table II-1, overall logarithmic beta and gamma decontamination factors of 6.9 and 6.6 were obtained, with ruthenium, for which an overall log decontamination factor of 5.8 was obtained, being the limiting fission product. This decontamination should be adequate, however, for 20% burnup fuel cooled for 120 days. The performance in this respect is similar to that observed in hexone extraction.

In the process the solvent appears to pick up zirconium and ruthenium activity, and reconditioning is required. After studies of a number

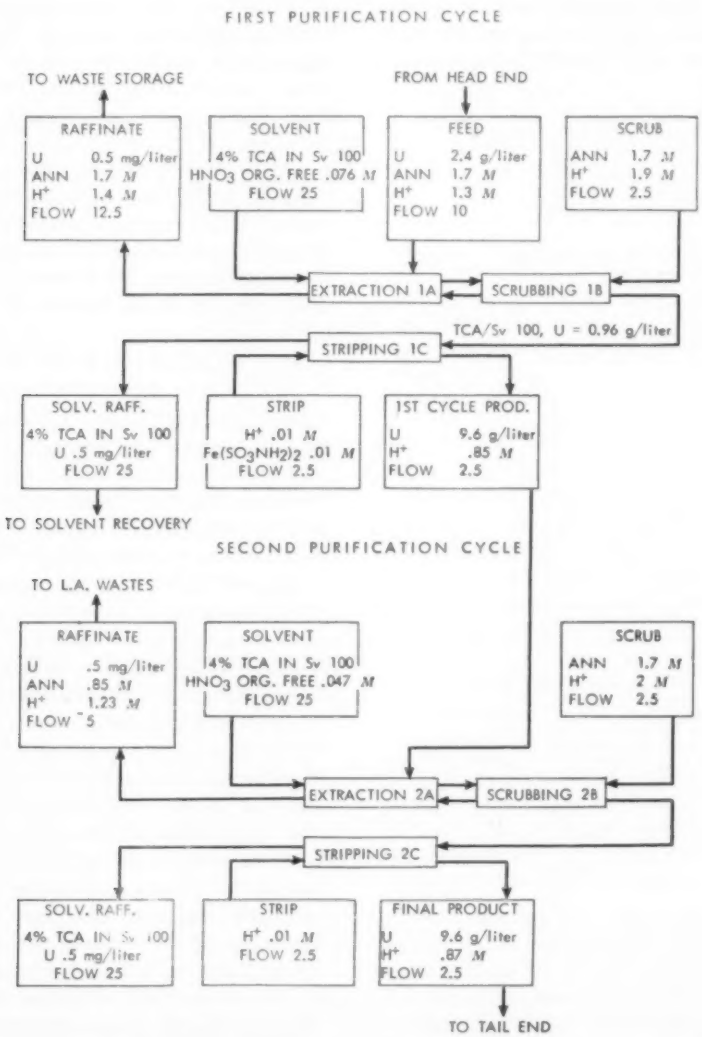

Fig. II-1 EUREX process chemical flow sheet for uranium-aluminum alloy.[8]

of possible wash solutions, treatment with 5M nitric acid followed by a dilute caustic wash was selected as most efficient. Separate wash systems will be used for the first and the second cycles. Radiolysis of the solvent was studied by two methods using a 6000-curie Co^{60} source. In one study a single exposure to 4×10^7 rads was given (calculated to be equivalent to 140 extraction cycles). Extensive amine conversion was observed, and decontamination from zirconium dropped drastically; a much smaller effect was observed when the irradiation was carried out in the presence of the aqueous feed solution. In the other study an irradiation cycle nominally equivalent to a single process cycle was followed by a solvent recovery cycle, and the process was repeated. After about 25 cycles (total dose: 2×10^7 rads), little change was observable in the solvent composition and performance. Conversion of tertiary to secondary amine was insignificant, the gross beta and gamma decontamination factors were unaffected, and the behavior of specific fission products did not show important variations. It was concluded that the use of tertiary amine solvents shows great promise but must be confirmed in plant operation.

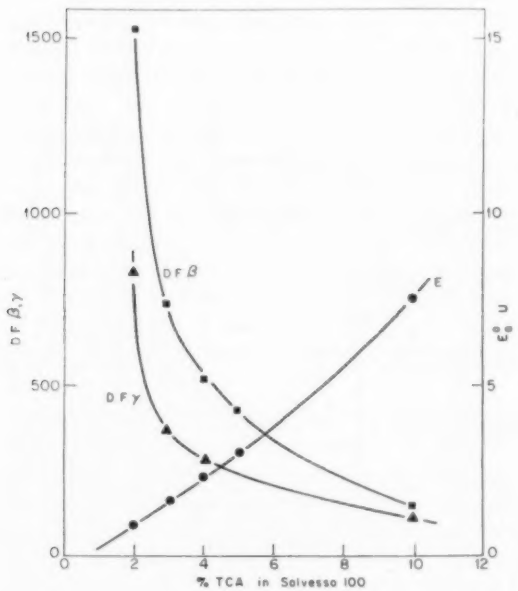

Fig. II-2 Effect of tricaprylamine concentration on uranium distribution coefficient and decontamination factor.[8] Aqueous phase: 1.4M HNO_3, 1.7M $Al(NO_3)_3$, 2.4 g of uranium per liter. Organic/aqueous = 1/1.

Table II-1 PRELIMINARY FISSION-PRODUCT DECONTAMINATION FACTORS[8]

Contactor	Log decontamination factors					
	Gross β	Gross γ	Cs	Rare earths	Ru	Zr
1st-cycle extraction	2.04	2.0	6	2.3	1.48	2.7
1st-cycle scrub				5	1.48	1.18
1st-cycle strip					1.21	1.12
Overall 1st cycle	5.3	5	6	7	4.17	5
2d cycle	1.6	1.6			1.6	1.6
Overall	6.9	6.6	6	7	5.77	6.6

Other Solvent Process Applications

Recent work related to miscellaneous uses of organic solvents in nuclear fuel processing has included the separation of fission products from beryllium by acetylacetone complexing and the decontamination of thorium by precipitating from solution in an organic phase.

Beryllium Purification

In Australia there is interest in a beryllium-moderated gas-cooled reactor. Processing of fuel is assumed to yield a raffinate containing valuable beryllium at perhaps 2M concentration, contaminated with considerable fission-product activity. It is desired to recover the beryllium in reusable form.

Aggett[12] has proposed that this might be accomplished with high efficiency in a single step by extracting the aqueous fission product–beryllium solution, complexed with ethylenediaminetetraacetic acid (EDTA), with acetylacetone in chloroform. The aqueous solution is first adjusted to a pH of 3.5 to 4.0 to minimize simultaneous rare-earth extraction; the presence of EDTA reduces zirconium extraction. The acetylacetone is used partly as its ammonium salt to neutralize hydrogen ions released by complex formation and maintain the pH approximately constant. Treatment is accomplished by refluxing the mixed phases for several hours. In tests of this simple procedure, it was found that, although the beryllium was decontaminated from cesium, strontium, and cerium by factors of about 10^4, the decontamination factor for zirconium was only about 70

and that for ruthenium was less than 8. Heating the solution with EDTA prior to extraction improved ruthenium decontamination very markedly and also improved zirconium separation. Since up to 94% of the beryllium was recoverable, it appears that such a process may have application.

Thorium Purification

The precipitation of thorium sulfate has long been used for the purification of thorium compounds. Rare earths and other metals in aqueous solutions are well separated by such means. Bril and deSaboia Araújo[13] have recently described a modification of this procedure in which the thorium as the nitrate is dissolved in TBP diluted with a hydrocarbon, and thorium sulfate is precipitated from the organic phase by bringing it into contact with a very slight excess of dilute sulfuric acid. Hydrated crystalline thorium sulfate precipitates readily, and the aqueous slurry is separated from the organic phase, filtered, and washed. Decontamination from most metals by factors of 100 or more is effected. Since in thorium fuel processing an organic phase saturated with thorium may be a product stream, thorium recovery by direct precipitation might be effected in a similar way.

New Solvents for Extraction Processes

Among solvent systems being studied for possible or broader application in the nuclear field are trioctylphosphine oxide (TOPO), bis (dialkylphosphinyl) alkanes, and *N,N*-dialkylamides.

Dialkylamides as Extractants

In recent work at Oak Ridge,[14] fourteen *N,N*-dialkylamides, prepared from amines and carboxylic acids and applied in diethylbenzene solution, were tested for their ability to extract uranium and thorium from nitrate systems in comparison with TBP and di-*sec*-butylphenyl phosphonate (D-*s*-BPP). The alkyl radicals ranged from methyl up to butyl and higher and included highly branched materials. The acid radicals ranged from caprylic to oleic and included a dibasic acid (phthalic). A comparison of the extraction coefficients for uranium and thorium obtained with certain of these materials over an acidity range from 2*M* to 8*M* is given in Fig. II-3.

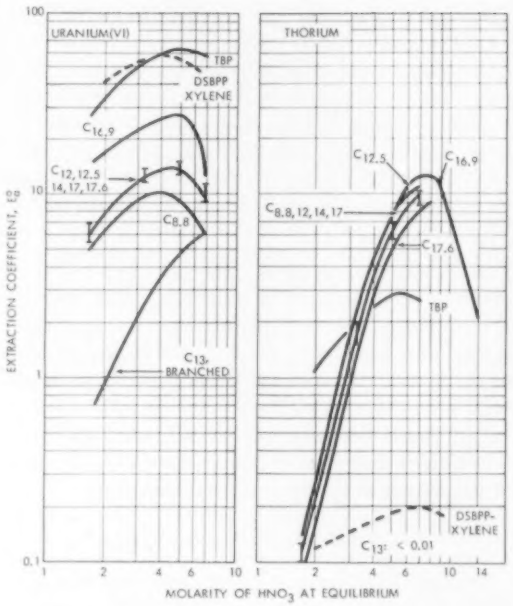

Fig. II-3 Uranium and thorium extraction from nitric acid by 1*M* solutions of *N,N*-dimethylamides in diethylbenzene.[14] (Code numbers are the average numbers of carbon atoms in the acid radicals of the amides. C_{13} is branched; all others are straight chain.)

Some of the unbranched alkyl chains had about the same extraction power for uranium and thorium. Branching of the alkyl chains usually caused a greater decrease in thorium extraction than in uranium extraction. Thorium extraction was characterized by a strong dependence on the acidity of the aqueous phase. The data suggest that thorium and uranium could be recovered separately or simultaneously by choosing the appropriate amide structure and nitric acid concentration. None of the amides gave uranium extraction coefficients as high as those obtained with TBP or D-*s*-BPP at the same concentration in the solvent. However, all the amides tested indicated uranium-thorium separations that were at least as good as those obtained with TBP.

Tributyl Phosphate (TBP) and Trioctylphosphine Oxide (TOPO) Complexes

Nadig and Smutz at Ames Laboratory have recently reported[15] an infrared spectra investigation of uranium, thorium, and rare-earth complexes of TBP and TOPO. The principal

data were obtained for nitrate systems, but some spectra were obtained for chloride and perchlorate systems also. The spectra indicated that, in all solute-solvent systems studied, a single complex was formed with the attachment of the solute taking place at the phosphoryl oxygen. There was no indication of an attachment to the oxygen of the P-O-C group in the case of TBP.

A linear correlation was obtained between the ionic potential of a solute in TBP and the P → O frequency shift. A different linear correlation was found for solutes in TOPO. It would be expected that the higher the ionic potenital of the solute the stronger the bond formed between it and the solvent. From theoretical considerations the shift is interpreted as indicative of the strength of the complex formed.

Bis (di-2-ethylbutylphosphinyl) Methane

Parker and Banks, also at Ames Laboratory, have reported further work on the complexing properties of gem-bis (disubstituted-phosphinyl) alkanes for heavy metals. The recent report concerns complexes of bis (di-2-ethylbutylphosphinyl) methane (EBDPM) with uranyl nitrate and with thorium nitrate.[16] In the course of studying the extraction of uranium and thorium by EBDPM in hexane, some solid complexes were isolated. These were examined with the hope of obtaining information on the nature of the extractable species. The complex with U(VI) was found to be a monomer, $UO_2(NO_3)_2$ (EBDPM), whereas the complex with thorium is a dimer, $[Th(NO_3)_4]_2$ $(EBDPM)_3$. Both complexes are of high thermal stability. It appears that in the complexes EBDPM acts as a bidentate ligand and the nitrato group is coordinated.

Chemical Processing in the Transuranic-Element Program

A group of 11 articles has recently appeared[17] in *Nuclear Science and Engineering* on all major aspects of AEC's program for the production of gram quantities of the higher transuranic elements. A large part of this program will be conducted at Oak Ridge National Laboratory (ORNL). General aspects of the program are outlined by Ferguson[18] and Burch et al.;[19] the special irradiation facility is described by Winters;[20] chemical processing techniques and problems are discussed by Leuze,[21] Lloyd,[22] and Baybarz;[23,24] fabrication methods are covered by Lotts et al.;[25] and the process facility design and equipment are reviewed by Unger et al.,[26] Nichols et al.,[27] and Yarbro et al.[28]

Burch et al.[19] note that the planned production of transuranium elements started with the irradiation of about 10 kg of Pu^{239} in Savannah River reactors, and that such irradiation will be continued to almost complete burnup. About 1 kg of Pu^{242}, Am^{243}, and Cm^{244} will be produced and initially separated by processing at Savannah River and Oak Ridge. Plutonium-242 as its oxide, and later the americium and curium isotopes, will be fabricated into cermet target rods with aluminum and irradiated in the High-Flux Isotope Reactor (HFIR) at Oak Ridge. Special processing and fabrication facilities (TRU facility) are being built at Oak Ridge, capable of operating with the intense alpha, gamma, and neutron radiations encountered in these operations. The cycles will be repeated, as shown in Fig. II-4, aiming at the production of 1 g of Cf^{252} by about 1968.

Leuze[21] described a procedure for processing the Savannah River-irradiated plutonium-aluminum alloy. Following dissolution of the alloy in nitric acid, plutonium is recovered from the solution and decontaminated by an anion-exchange process. Americium, curium, and rare earths in the raffinate may be separated by sorption from a neutral aluminum nitrate solution on anion-exchange resin, followed by nitric acid elution. After nitrate removal and conversion to chloride salts, the americium and curium present may be separated from the rare earths by extraction from concentrated lithium chloride solution with a tertiary amine[23] (Alamine 336). An alternate procedure for separation of americium and curium actually used at Savannah River involves double sulfate precipitation. The crude nitric acid solution of americium, curium, and rare-earth fission products was shipped to Oak Ridge for further processing.[29]

Following irradiation of Pu^{242}, Am^{243}, Cm^{244}, and heavier isotopes in the HFIR, the targets will be dissolved in hydrochloric acid and actinides will be recovered by tertiary amine extraction from concentrated lithium chloride solution, essentially as described above. Decay heat and radiation are major problems, even

with the few grams of transuranic elements involved in handling each target. At two days decay an irradiated californium target is calculated to emit 250 watts, and the process will require 4.5 ft of dense concrete for gamma and neutron shielding.

The actinides separated by tertiary amine extraction will be split into two fractions by extracting the transuranium elements—berkelium, californium, einsteinium, and fermium—into 2-ethylhexylphenyl phosphonic acid from tract this solution with dilute TBP, after neutralization of the raffinate, in order to separate americium, curium, and the rare earths from alumium and the bulk of the fission products. Americium-curium purification was then to be accomplished by sorption of these isotopes and the rare earths from an 8*M* lithium nitrate solution, from which rare earths would first be eluted with 10*M* lithium chloride. Americium-curium elution would then be effected with 1.0*M* lithium chloride. Small-scale tests indicated

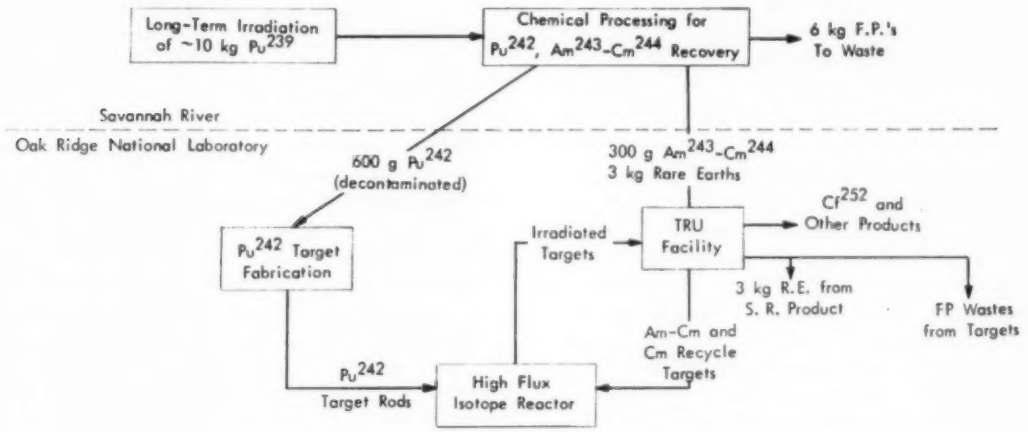
Long-Term Irradiation of ~10 kg Pu^{239}
Chemical Processing for Pu^{242}, Am^{243}-Cm^{244} Recovery
6 kg F.P.'s To Waste
Savannah River
Oak Ridge National Laboratory
600 g Pu^{242} (decontaminated)
300 g Am^{243}-Cm^{244} 3 kg Rare Earths
Cf^{252} and Other Products
Pu^{242} Target Fabrication
Irradiated Targets
TRU Facility
3 kg R.E. from S. R. Product
FP Wastes from Targets
Am-Cm and Cm Recycle Targets
Pu^{242} Target Rods
High Flux Isotope Reactor

Fig. II-4 Overall transuranium production scheme.[19]

about 1*M* hydrochloric acid solution.[24,30] The heavier elements will be stripped from the solvent with 5*M* to 6*M* hydrochloric acid. The major break in extractability between curium and berkelium makes this an excellent system for this separation. The berkelium-curium separation factor is about 30. Separation factors between other adjacent actinides are only 1.3 to 3.3.

Berkelium may be separated from other actinides by oxidizing to the tetravalent state and extracting with diethylhexyl phosphoric acid. Attractive solvent-extraction processes to separate transcalifornium isotopes do not appear to be available. Chromatographic elution from a cation-exchange resin has been used.

Several alternative methods for the recovery and purification of americium and curium from waste streams for Pu^{242} recovery have been developed.[31] Earlier, it was proposed to recover plutonium by solvent extraction from an acidic aluminum nitrate solution and to further ex-

that more than 99.5% of the americium and curium was recoverable with no rare earths detectable by oxalate precipitation tests.

The processing technique for this purpose (Fig. II-5) now described by Lloyd[22] involves starting with a waste resulting from ion-exchange recovery of Pu^{242}. The strongly acid aluminum nitrate waste stream, containing small amounts of fluoride, sulfate, and other metals, is boiled down to remove as much acid as possible, adjusted to the maximum usable aluminum concentration, and then filtered. Americium, curium, and rare earths are then sorbed from this stream by Dowex 1 anion-exchange resin. The resin is washed with 8*M* lithium nitrate, and the actinide and lanthanide elements are eluted with dilute nitric acid. The separation of these groups will then be effected by tertiary amine extraction from a lithium chloride system.[23,29] In a small-scale demonstration run with plutonium waste, an americium-curium recovery of 99.4% was obtained in the ion-

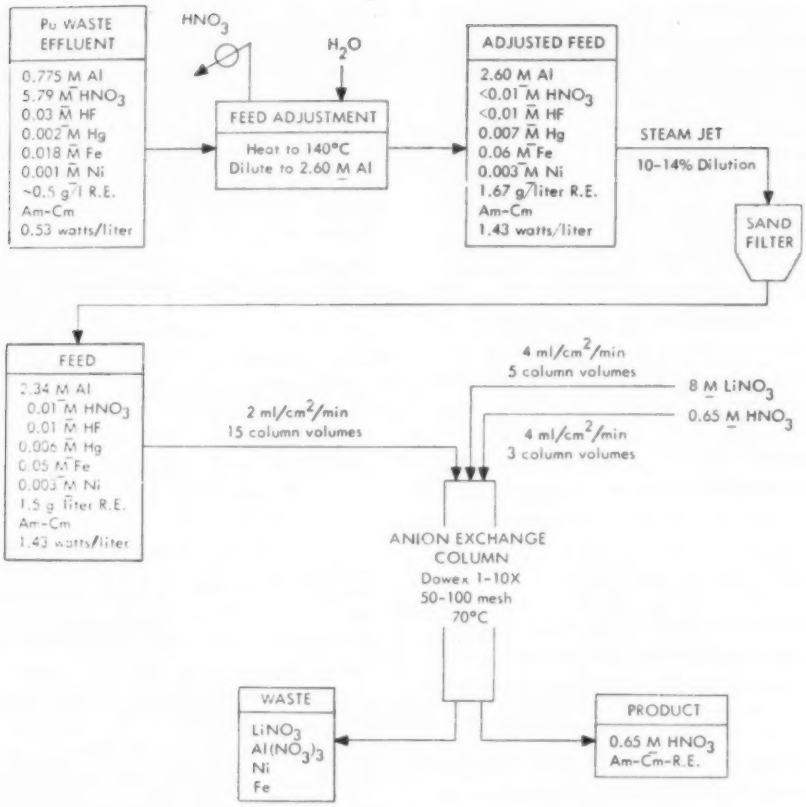

Fig. II-5 Recovery of americium and curium from plutonium process waste.[22]

exchange step, and decontamination factors of 20 to 500 were obtained for ruthenium, antimony, zirconium, and cesium. (C. E. Stevenson)

Recovery of Neptunium from Solvent Processes

Plutonium-238 is currently being used in increasing amounts as an energy source for space vehicles expected to be in service over a long period. Such use is favored because of its relatively high specific output (0.55 watt/g from emission of 5.4-Mev alpha particles), minimal shielding requirement, and long half-life (about 90 years). It is produced at the rate of several kilograms per year by irradiation and processing of Np^{237}, whose source in part is the processing of irradiated natural- and enriched-uranium fuels at the Hanford and Savannah River separations plants. The processing methods used were recently described at the initial symposium[32] sponsored by the newly formed Division of Nuclear Chemistry and Technology of the American Chemical Society at a national meeting of the society at Denver, Colo. The symposium includes 12 papers from ORNL, the Hanford Atomic Products Operation (HAPO) of the General Electric Company, the Savannah River Plant of E. I. du Pont de Nemours & Co., Inc., and the Mound Laboratory, operated by Monsanto. The latter three organizations participate actively in the program. Neptunium recovered and decontaminated at Hanford and Savannah River is fabricated into targets, further irradiated, and processed for plutonium recovery and decontamination at Savannah River. Mound Laboratory prepares metal from the purified plutonium solution.

The papers describe the methods of Np^{237} recovery as a by-product of the application of

conventional separations processes to uranium-based nuclear fuels. Efficient recovery is achieved even though the neptunium is initially present at concentrations very much below those of, for example, plutonium in such fuels. The economics of doing this depend, of course, on the costs of the additional equipment, labor, and materials required and on the value of the neptunium and plutonium recovered.

Neptunium-237 results from the decay of U^{237}, produced either by the successive capture of two neutrons by U^{235} or by an $(n,2n)$ reaction on U^{238}. The former reaction is generally the more important, although, in reactors fueled with natural or slightly enriched uranium, the amount of neptunium derived from U^{238} may be comparable to that from U^{235}, depending on initial enrichment or burnup. Lane, Vondy, and Gresky[32a] report calculations indicating a potential recovery of several kilograms per year of Np^{237} per 1000 Mw(t) from typical pressurized- and boiling-water power reactors. By reirradiation, separation, and recycling, the bulk of this can be converted to Pu^{238} in several passes. If a value of $100/g is assumed for Np^{237}, the gross value of the latter might amount to of the order of 0.1 to 0.3 mill/kw-hr. The recovery costs are not given and may be high because of the type of operations involved; thus the net effect as a power credit is uncertain.

Methods for recovery of neptunium from natural-uranium solvent-extraction cycles at Hanford and Savannah River generally involve either its diversion to a waste stream, with or without prior accumulation in process, or diversion to a supplementary extraction cycle for accumulation and intermittent recovery. A similar method is used for enriched uranium at Savannah River. The direction of neptunium partition is accomplished by acidity regulation, salting effects, and valence adjustment with nitrite and ferrous sulfamate.

Judson[32b], in discussing Hanford operations, reports that in the Purex (TBP) process neptunium is carried along with uranium after partition of plutonium and remains with the aqueous waste stream after extraction of uranium in the second cycle. After concentration, two-thirds of this stream is returned to the first-cycle extraction column, as waste back-cycle, where the neptunium is again picked up with uranium, and the remaining third is diverted to a pair of extraction columns, operating as a neptunium accumulation cycle. Periodically, the latter cycle is operated for neptunium decontamination and product removal. With such a procedure, there is no interference with normal process operations, and the bulk of the neptunium is retained in a system where it is not exposed to the possibility of loss with the principal aqueous waste. A recovery of over 80% of the neptunium is accomplished, and it is decontaminated by a factor greater than 10^6 from uranium, and 10^8 from significant fission products.

The package solvent-extraction unit, which was installed remotely in the Purex Canyon, was described by Duckworth and Michels.[32c] Construction and installation details have been given previously.[33]

In the Hanford Redox process, which was converted from an acid-deficient feed system to an acid feed system to permit neptunium recovery, neptunium is extracted into hexone solvent, along with uranium and plutonium in the codecontamination column system, and is then separated and forced into the aqueous raffinate stream and returned to the first-cycle scrub column. Neptunium is accumulated by recycling between the two systems. It is periodically removed from the scrub column by a water strip and is transferred to a special pair of columns for decontamination from uranium, plutonium, and fission products. Neptunium-recovery capabilities are greater than 90% of that present in the feed, and decontamination factors for the process (including an ozonization step) are greater than 10^6 for uranium, ruthenium, and other major fission products.

Neptunium recovered from both processes is purified by batch ion exchange after concentration and adjustment to the tetravalent state by ferrous sulfamate stabilized with hydrazine. It is loaded onto Dowex 21SK resin from 6M nitric acid and scrubbed with additional acid, and with 8M acid containing fluoride, to remove plutonium and fission products. The fluoride is then washed out with 8M acid, and the product is eluted with 0.35M acid. Further decontamination by factors of the order of 1000 or more is obtained in this process. The remotely operated ion-exchange system used was described by Duckworth and LaRiviere.[32d]

At Savannah River, Purex processing of natural uranium has been modified only by the addition of nitrite to the next to the last stage of the first-cycle mixer-settler extractor to maintain neptunium in the inextractable penta-

valent state and minimize its refluxing to the main process. As described by Poe,[32g] neptunium is then recovered by anion exchange from the high activity first-cycle aqueous waste, after adjusting to the adsorbable tetravalent state with ferrous sulfamate stabilized with hydrazine. A novel type of agitated ion-exchange column is used to permit operation with an unfiltered feed containing solids, and ready removal and replacement of the resin by remote techniques. The development of this type of column was described by Caracciolo.[32h] With three such beds in series, a recovery of greater than 90% is attained, and the overall decontamination factor averages about 5000. Further decontamination and separation from plutonium is accomplished by additional stages of ion exchange. Recovery and purification of neptunium from processing of enriched uranium is accomplished by solvent extraction. Neptunium is maintained in the tetravalent state with ferrous sulfamate and is extracted in the first-cycle mixer-settler extractor and partitioned in the IB mixer-settler, as plutonium is separated in Purex processing. The neptunium is then decontaminated by a second cycle of extraction in equipment normally used for plutonium processing. For accumulation and concentration, the neptunium product may be recycled to the second-cycle feed.

The production of neptunium dioxide by oxalate precipitation, following adjustment to the tetravalent state with ascorbic acid, and subsequent calcination of the precipitate, was described by Porter.[32e] Peroxide precipitation was also investigated but was found to be more sensitive to process variables and the peroxide precipitate was not so easily filtered. Neptunium dioxide is then blended with Alcoa type 101 alunium powder (13.5–23% NpO_2 in the mixture), and a compact is formed by pressing in a die at 20 tsi. Folger[32f] noted that the compacts are prepared for irradiation by placing them in an aluminum can, heating at 600 to 620°C under pressure to metallurgically bond the compacts to the can, and welding a plug into the top of the can. There was some indication of solid-state reduction of neptunium in this operation.

Following irradiation and several weeks decay, Pu^{238} is separated from neptunium by an ion-exchange process (described by Burney[32i]) following dissolution of the targets in nitric acid in the presence of low concentrations of mercuric and fluoride ions. A three-cycle ion-exchange process is used, in which the separation of plutonium from neptunium is effected in the second cycle by reducing plutonium from the tetravalent to the trivalent state by eluting with 5.5 *M* nitric acid containing ferrous sulfamate and hydrazine. Both neptunium and plutonium products are then purified by another ion-exchange cycle. Dowex 1 and Permutit SK anion-exchange resin are used. The former provides higher decontamination from fission products, but the latter is more stable under alpha radiation and has been used in the Pu^{238} column. Dukes[32k] has described analytical methods used in connection with these processes.

Metal is then produced at Mound Laboratory from the recovered Pu^{238} by oxalate precipitation, conversion to fluoride, and bomb reduction. The processes and equipment used for this purpose were described by Griffo.[32j] Particular problems in this operation are the high rate of generation of neutrons by the fluoride salt, and the very considerable decay heat of the metal, which required special provisions for cooling in storage.

Rogers and Brown[32l] presented information about specific compounds of Pu^{238}.

Plant and Equipment Design

Aqueous processing is to play a very important role in the extensive transuranium program at ORNL. Proposed processes were described in the preceding section. The following two papers describe the Transuranium Processing Plant and equipment. Unger[26] et al. describe the processing facility, and Yarbro[28] et al. describe the equipment.

The following requirements served as the basis for establishing design criteria: The TRU facility is required to process and fabricate one HFIR target per week; to provide shielded storage facilities for up to 4 g of Cf^{252} and the other transuranium elements produced by the curium rod irradiations, as well as those produced by special irradiation of, for instance, 1 g of californium; to provide massive shielding adequate for a point source of 3×10^{12} fission neutrons/sec; and to provide facile equipment replacement and revision without sacrifice of the containment standards exacted by the toxicity of the emitting actinides.

The TRU building facility[26] will consist of nine heavily shielded cells, served by master-slave manipulators, and eight laboratories arranged as shown in Figs. II-6 to II-8.

The shielded process cells are arranged in line. Removable top plugs provide access, and the top and back of the cell line is served by a bridge crane in a limited-access part of the building. The front face of the cells is provided with windows, master-slave manipulators, and plugged ports for possible periscope installation. The cells are shielded by 54 in. of magnetite concrete.

Equipment will be enclosed in a nonremovable cell cubicle formed on the front and sides by the cell walls, and of epoxy resin-coated stainless-steel plate on the rear wall and top. The bottom is of Hastelloy C to withstand possible corrosion from chloride solution spills. The cubicle atmosphere is recycled at 350 cfm through absolute filters and a cooler.

A shielded tank pit is behind and below the cell for storage of removable process equipment and waste collection equipment. This pit has a Hastelloy C floor and walls of fiber-glass resin. The tank pit may be flooded for maintenance of the equipment.

Communications between cells and the transfer area is by a conveyor consisting of a canister (8 in. in diameter by 8 in. high inside) on a dolly drawn by a double chain. The canister can be elevated by differential motion of the chains and will seal to a mating door in a cubicle floor. A 12- by 12-in. air lock in each wall allows transfer between adjacent cells. A shielded carrier may be introduced into the transfer area (Fig. II-6) for removal of samples, etc.

The high specific toxicity of the transuranic elements (4×10^{10} body burdens/g for Cf^{252}) requires special provisions to ensure against escape of material. The process equipment will be operated at −10 in. of water gauge, the alpha-

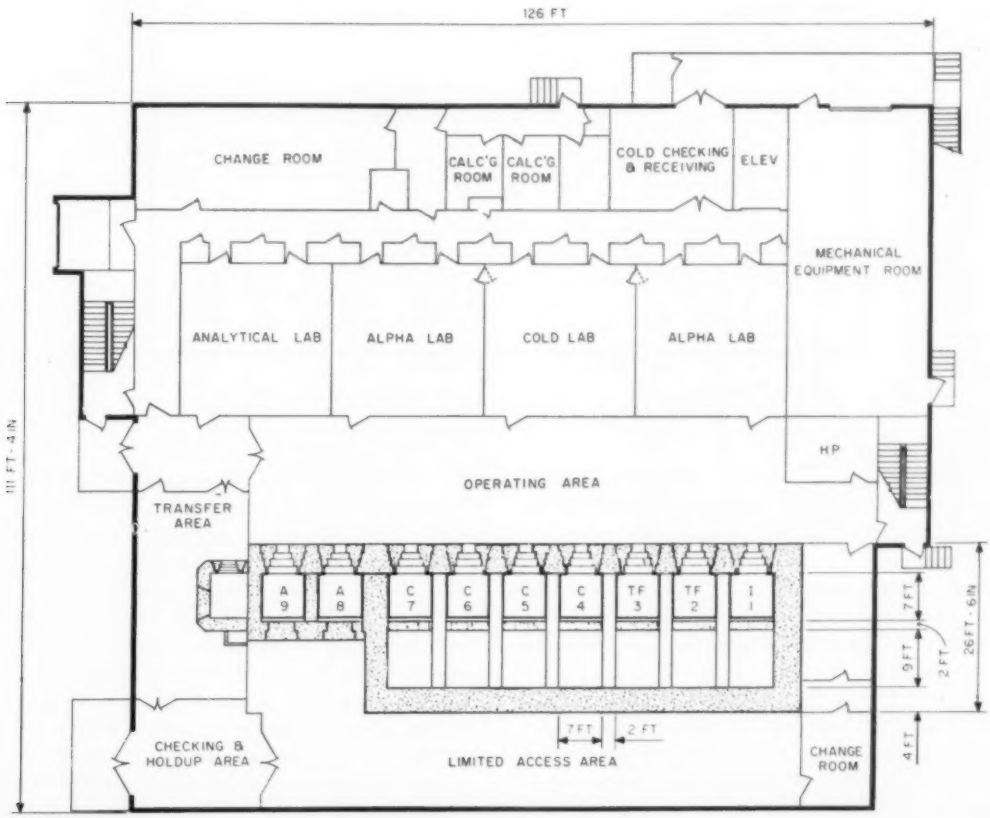

Fig. II-6 Transuranium processing facility—first-floor plan.[26]

tight cubicles at −1.7 in., the cell at −1.4 in., and the building at −0.3 in. Air is supplied from nonradioactive corridors toward areas of higher contamination potential and is exhausted through roughing and absolute filters to the roof. Purge air to the cubicles and other envelopes within the building is filtered through three sets of filters, two of which are of the absolute type.

chanical equipment such as pumps, valves, and solvent contactors will be in cubicles located in process cells 4 through 7. Cell 7 contains equipment for dissolution and feed preparation, ion exchange for plutonium recovery, and first-cycle solvent extraction (pulse columns). Cell 6 contains second-cycle solvent-extraction equipment for separating americium-curium from

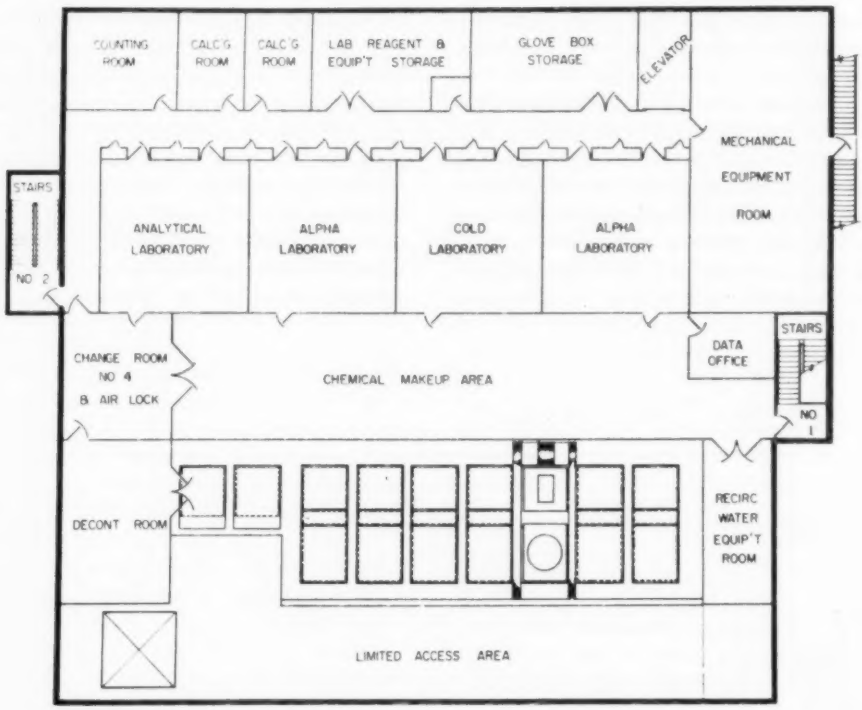

Fig. II-7 Transuranium processing facility—second-floor plan.[26]

Vessel off-gas is caustic scrubbed before going to the filter. All exhaust except building air is discharged to the atmosphere through a 250-ft stack.

Waste liquids are collected in fairly conventional manner, with small holdup tanks being used where there is a possibility of rework being required.

The projected cost is reported as about $6 million for the building and general equipment and about $2.5 million for process and target fabrication equipment. Full-scale operation is scheduled for December 1965.

The second paper[28] covers some of the specific designs for the proposed equipment. Me-

the higher actinides. Equipment for purification of berkelium from the other actinides by batch solvent extraction is included, as well as other equipment under development for rough separation of californium from einsteinium and fermium (Fig. II-9). Product storage tanks and equipment for further separations and purification of main line products are located in cell 5. Cell 4 contains equipment for the preparation of the actinide oxides for use in pellet and target fabrication in cubicles 1 through 3.

The development of a simple all-metal piping disconnect (Fig. II-10) has served to facilitate remote replacement techniques required because of severe corrosion and activity condi-

tions. The connector for $\frac{3}{8}$- to $\frac{3}{4}$-in. tubing consists of two conical surfaces (18° male, 20° female angle) forced together by a clamp. The single bolt on the disconnect clamp may be turned by an impact wrench or a long-handled socket wrench. Tests indicated leakage rates of less than 1×10^{-8} standard cm^3/sec of helium after several connects and disconnects of the coupling. It was also possible to have 1° misalignment. The fitting stood up well under simulated corrosion conditions (0.049-in. wall thickness tubing failed while mating surfaces remained leaktight).

A diaphragm pump has been developed which is fabricated of Hastelloy C or zirconium, depending on the process solution it pumps. Double ball checks are used, and the diaphragm is pulsed by alternately applying pressure and vacuum. The pump is 6 in. in diameter and 1.5 in. thick with a capacity of 30 to 40 liters/hr.

A prototype design of a compact air-operated valve has been developed and tested, but refinements are required to overcome problems in welding Hastelloy C or Zircaloy-2.

All the mechanical equipment will be mounted on racks in the cubicles with sampling and service connections provided. Details are given for some typical arrangements. Extensive corrosion tests were run on various metals with simulated process solutions including $3M$ to $10M$ hydrochloric acid and various nitric-hydrochloric acid mixtures, at solution temperatures from 35 to 130°C. Tantalum showed corrosion rates less than 1 mil/year in all cases but will only be used where Zircaloy-2 or Hastelloy C cannot be used because of cost and fabrication difficulties. Both Zircaloy-2 and Hastelloy C showed satisfactory corrosion for some of the processing solutions. Hastelloy C is proposed for the bulk of the process piping. The effects of alpha activity on corrosion indicated an accelerated rate, probably not due to direct effects but to a secondary effect, such as the production of peroxide and ozone.

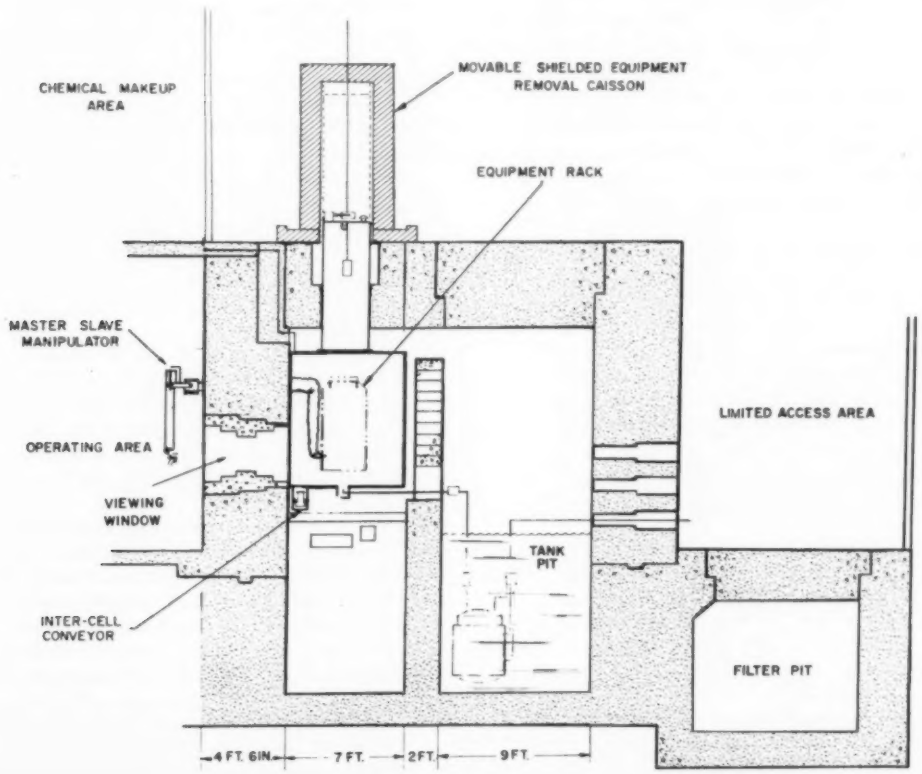

Fig. II-8 Transuranium facility cell cross section.[26]

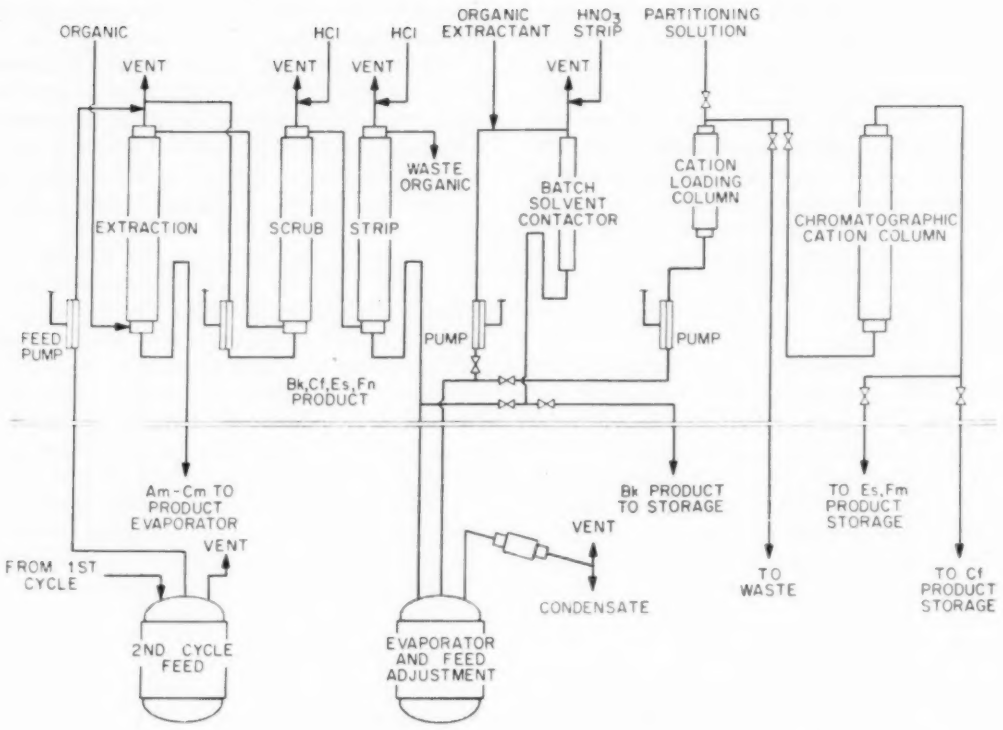

Fig. II-9 Equipment flow sheet, cell 6, transuranium processing facility.[28]

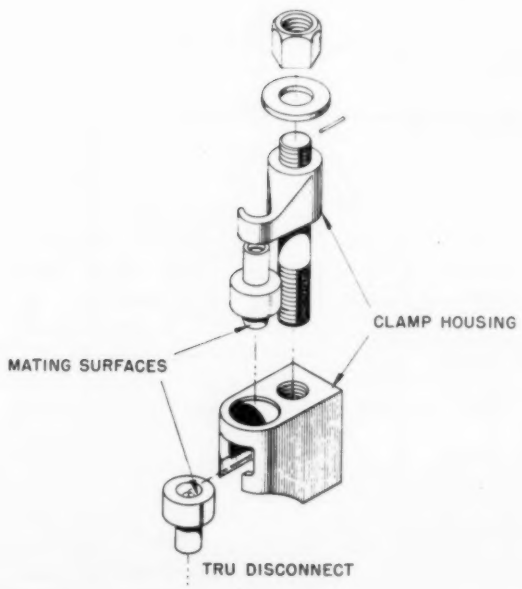

Fig. II-10 TRU piping disconnect.[28]

Basic mockups will be made and, when proved out, will be moved into the cells. (D. M. Paige)

References

1. *Reactor Fuel Process.*, 6(2): 6 (April 1963).
2. B. J. Newby, An Improved Process for Zirconium Alloy Nuclear Reactor Fuels. Part II. Continuous Dissolution with 5M Hydrofluoric Acid, USAEC Report IDO-14619, Phillips Petroleum Co., Sept. 25, 1963.
3. J. A. Buckham, Idaho Chemical Processing Plant, October and November 1963. (Unpublished)
4. *Reactor Fuel Process.*, 4(4): 33 (October 1961).
5. T. A. Gens, Laboratory Development of a Combined Chloride Volatility–Aqueous Processing Method for Uranium-Zirconium Fuels, USAEC Report ORNL-TM-645, Oak Ridge National Laboratory, Oct. 15, 1963.
6. C. F. Coleman, Amines as Extractants, *Nucl. Sci. Eng.*, 17: 274-286 (October 1963).
7. W. E. Keder and A. S. Wilson, Amines as Extractants—Studies of the Organic Phase, *Nucl. Sci. Eng.*, 17: 281-297 (October 1963).

8. F. Baroncelli, G. Calleri, A. Moccia, G. Scibona, and M. Zifferero, The Eurex Process: Processing of Irradiated U-Al Alloys by Amine Extraction, *Nucl. Sci. Eng.*, 17: 298-308 (October 1963).
9. *Reactor Fuel Process.*, 6(1): 8 (January 1963).
10. H. A. C. McKay, R. J. W. Streeton, and A. G. Wain, Mixer-Settler Runs to Study Uranium(IV) as a Reductant in Uranium/Plutonium Separation, British Report AERE-R-4381, September 1963.
11. *Reactor Fuel Process.*, 6(2): 10 (April 1963).
12. J. Aggett, Separation of Beryllium from Fission Products in a Nitrate Medium — Preliminary Experiments Using Solvent Extraction, Australian Report AAEC/TM-187, March 1963.
13. K. J. Bril and P. G. deSaboia Araûjo, Decontamination of Thorium Direct Precipitation of Thorium Sulfate from Thorium Nitrate Solutions in Tributyl Phosphate, *Ind. Eng. Chem., Process Design Develop.*, 3: 8 (January 1964).
14. K. B. Brown, Chemical Technology Division, Chemical Development Section C, Progress Report on Separations Chemistry and Progress Research for January–June 1963, USAEC Report ORNL-3496, Oak Ridge National Laboratory, Oct. 25, 1963.
15. E. W. Nadig and M. Smutz, Metal Nitrate Complexes with Tributyl Phosphate and Trioctyl Phosphine Oxide, USAEC Report IS-595, Ames Laboratory, February 1963.
16. J. R. Parker and C. V. Banks, Gem-Bis (disubstitutedphosphinyl) Alkanes. III. Crystalline Complexes of Bis (di-2-ethylbutylphosphinyl) Methane with Uranium(VI) Nitrate and with Thorium Nitrate, USAEC Report IS-560, Ames Laboratory, Oct. 16, 1962.
17. ORNL Transuranium Program, *Nucl. Sci. Eng.*, 17: 435-497 (November 1963).
18. D. E. Ferguson, The Production of Transuranium Elements, *Nucl. Sci. Eng.*, 17: 435-437 (November 1963).
19. W. D. Burch, E. D. Arnold, and A. Chetham-Strode, Production of the Transuranium Elements, *Nucl. Sci. Eng.*, 17: 438-442 (November 1963).
20. C. E. Winters, The High Flux Isotope Reactor, *Nucl. Sci. Eng.*, 17: 443-447 (November 1963).
21. R. E. Leuze, Chemical Processing Requirements for Transuranium Element Recovery, *Nucl. Sci. Eng.*, 17: 448-451 (November 1963).
22. M. H. Lloyd, An Anion Exchange Process for Americium-Curium Recovery from Plutonium Process Waste, *Nucl. Sci. Eng.*, 17: 452-456 (November 1963).
23. R. D. Baybarz, B. S. Weaver, and H. B. Kinser, Isolation of Transplutonium Elements by Tertiary Amine Extraction, *Nucl. Sci. Eng.*, 17: 457-462 (November 1963).
24. R. D. Baybarz, Separation of Transplutonium Elements by Phosphonate Extraction, *Nucl. Sci. Eng.*, 17: 463-467 (November 1963).
25. A. L. Lotts, W. C. Thurber, M. K. Preston, Jr., and D. A. Douglas, Jr., Development of Procedures and Equipment for Fabrication of the High Flux Isotope Reactor Target Rods, *Nucl. Sci. Eng.*, 17: 468-477 (November 1963).
26. W. E. Unger, B. F. Bottenfield, and F. L. Hannon, Transuranium Processing Facility Design, *Nucl. Sci. Eng.*, 17: 478-485 (November 1963).
27. J. P. Nichols, E. D. Arnold, and D. K. Trubey, Evaluation of Shielding Hazards in the Transuranium Processing Plant, *Nucl. Sci. Eng.*, 17: 486-491 (November 1963).
28. O. O. Yarbro, J. L. English, and T. S. Mackey, Process Equipment Design and Development for the Transuranium Processing Plant, *Nucl. Sci. Eng.*, 17: 492-497 (November 1963).
29. Savannah River Laboratories, private communication, Mar. 6, 1964.
30. *Reactor Fuel Process.*, 5(4): 16 (October 1962).
31. M. H. Lloyd and R. E. Leuze, Anion Exchange Separation of Trivalent Actinides and Lanthanides, *Nucl. Sci. Eng.*, 11: 274-277 (1961).
32. Symposium on Production Technology of Np^{237} and Pu^{238}, sponsored by Division of Nuclear Chemistry and Technology, 146th National American Chemical Society Meeting, Denver, Colorado, January 20–21, 1964.
    a. J. A. Lane, D. R. Vondy, and Arnold T. Gresky, The Production of Np^{237} and Pu^{238} in Thermal Power Reactors, Oak Ridge National Laboratory.
    b. R. E. Isaacson and B. F. Judson, Neptunium Recovery and Purification at Hanford, General Electric Company, Hanford Atomic Products Operation.
    c. J. P. Duckworth and L. R. Michels, New Neptunium Recovery Facility at the Hanford Purex Plant, General Electric Company, Hanford Atomic Products Operation.
    d. J. P. Duckworth and J. R. LaRiviere, New Neptunium Purification Facility at the Hanford Purex Plant, General Electric Company, Hanford Atomic Products Operation.
    e. J. A. Porter, Production of Neptunium Dioxide, E. I. du Pont de Nemours & Co., Inc. (to be published in *Ind. Eng. Chem. Process Design Develop.).*
    f. R. E. Myrick and R. L. Folger, Fabrication of Targets for Neutron Irradiation of Neptunium Dioxide, E. I. du Pont de Nemours & Co., Inc. (to be published in *Ind. Eng. Chem. Process Design Develop.).*
    g. A. W. Joyce, Jr., R. I. Martens, and W. L. Poe, Jr., Np^{237} and Pu^{238} Separation at the Savannah River Plant, E. I. du Pont de Nemours & Co., Inc. (to be published in *Ind. Eng. Chem. Process Design Develop.).*
    h. V. P. Caracciolo, An Ion Exchange Column for Remote Operation in a Radiochemical Separa-

tions Plant, E. I. du Pont de Nemours & Co., Inc. (to be published in *Ind. Eng. Chem. Process Design Develop.).*

i. G. A. Burney, An Ion Exchange Process for the Recovery of Pu^{238} from Irradiated Np^{237}, E. I. du Pont de Nemours & Co., Inc. (to be published in *Ind. Eng. Chem. Process Design Develop.).*

j. J. S. Griffo and F. D. Lonadier, Production of Plutonium-238 Metal, Monsanto Research Corp.

k. E. K. Dukes and R. S. Dorsett, Determination of Plutonium-238 and Neptunium-237 in Process Solutions, E. I. du Pont de Nemours & Co., Inc. (to be published in *Ind. Eng. Chem. Process Design Develop.).*

l. D. R. Rogers and W. B. Brown, Potassium Plutonium Sulfate as a Primary Standard for Plutonium-238, Monsanto Research Corp.

33. *Reactor Fuel Process.*, 7(1): 16 (Winter 1963–1964).

Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Nitrofluor Process

The Nitrofluor process for treating spent reactor fuel is based on fuel dissolution or disintegration in anhydrous NO_2-HF solutions and final recovery of uranium and plutonium as volatile hexafluorides. A solution containing 15 mole % NO_2 in HF appears to be particularly suitable for fuels containing uranium dicarbide particles coated with a layer of pyrolytic carbon. The carbon matrix of the coating is disintegrated by the solution, and the coating is split open, allowing the uranium carbide within to be dissolved. Nearly complete dissolution of uranium (95%) has been achieved[1] by reacting the carbide fuel material in 15 mole % NO_2–85 mole % HF solution for 3 hr at 140°C. The uranium-bearing solution is filtered through 15-μ sintered nickel, removed from the dissolver, and evaporated to dryness.

Two methods have been employed successfully in the recovery of uranium from the residue. Treatment of the residue with BrF_3 at 200°C for 2 hr resulted in the volatilization as UF_6 of all but 0.3% of the uranium. In the second method the evaporator residue was contacted with NOF·3HF vapor at 400°C. In a 3.5-hr period, all but 0.8% of the uranium in the residue was volatilized. The uranium was collected as UF_4 in a downstream condenser maintained at room temperature.

An alternative solvent, NOF·3HF, is being evaluated for the dissolution step of the Nitrofluor process, since it offers the advantage of being less corrosive than the NO_2-HF solvent. Another advantage results from the fact that the boiling point (95°C) of the NOF·3HF azeotrope is 40°C higher than that of 15 mole % NO_2–85 mole % HF solution, thereby permitting fuel dissolution at considerably lower operating pressures.

Uranium dioxide readily dissolves in NOF·3HF; however, an excess of solvent is required to prevent precipitation of the $NOUF_6$ formed. Excessive solvent consumption is avoided by recycling a portion of the solvent after the $NOUF_6$ has been separated by evaporation of the solvent. A series of dissolution tests was performed[1] to determine the effect of solvent recycle on UO_2 dissolution rates. It was observed that after five solvent recycles the UO_2 dissolution rate decreased markedly. Concurrently, the corrosion rate of Monel alloy 400 increased with progressive solvent recycle.

The volatilization of $NOUF_6$ in the presence of NOF gas, or the vapor from NOF·3HF, is of considerable interest as a method for purifying uranium. Previous work[2] has shown that UO_2, UF_4, and UO_2F_2 are completely converted to a volatile compound in the presence of gaseous NOF at 400°C, presumably because the compounds were converted to $NOUF_6$ by NOF. A series of experiments has been performed[1] to define the conditions under which uranium is volatile in NOF environments. It was observed that the transfer of pure $NOUF_6$ is readily accomplished at 435°C in a flowing stream of NOF at 150 to 400 mm Hg abs. pressure. Uranium tetrafluoride was identified as the solid that results from the decomposition of the volatile compound in a downstream zone maintained at 400°C. The vapors from NO_2-HF solution produced an effect similar to that of NOF vapor, but the fraction of uranium volatilized was significantly less. No vaporization of uranium was observed when $NOUF_6$ was heated to 420°C in an inert atmosphere.

Molybdenum, which forms a nitrosyl salt ($NOMoF_6$), was shown to be volatile in NOF gas at 450°C. However, unlike the uranium homolog,

the molybdenum salt volatilized completely at 450°C in an atmosphere of helium. This behavior suggests that it may be possible to remove molybdenum preferentially from uranium by heating the complex salts resulting from evaporation of the Nitrofluor solvent after dissolution of the fuel material.

The volatility of niobium was tested using the salt prepared by dissolution of niobium metal in NOF·3HF. Complete niobium volatilization from the salt occurred when the salt was contacted with flowing NOF vapor at 428°C. No transfer of niobium was observed when helium was employed as the sweep gas. Similar survey tests have indicated that ruthenium and aluminum do not form volatile compounds in the presence of NOF gas at 450°C.

Volatility Processes for High-Enriched Fuels

The methods employed in the processing of reactor fuels containing highly enriched uranium differ from those used for low-enriched fuels in two major respects: (1) since the concentration of uranium in the fuel is low (<20%), the initial step of the processing scheme involves the separation of uranium from the fuel matrix, thereby freeing the uranium for subsequent recovery by volatility methods; and (2) recovery of plutonium is not required for highly enriched fuels. Several processes that involve separation methods based on the relative volatility of chlorides are being developed for the processing of reactor fuels containing enriched uranium. Studies are currently being made on zirconium alloy fuels. Initial separation of uranium from the alloy is achieved by converting the alloying metal to a volatile chloride. Final recovery of uranium is achieved by fluorination to produce volatile uranium hexafluoride. Volatility processes are also being applied to graphite-matrix reactor fuels containing enriched uranium carbide.

Zirconium-Uranium Alloy Fuels. A fluid-bed volatility process for the recovery of uranium from highly enriched uranium alloy fuels is being developed at Argonne National Laboratory (ANL).[3] Current studies are being made with zirconium alloy fuels. The process is based on the use of hydrogen chloride, at a temperature of 400°C, to convert the zirconium-uranium alloy to volatile zirconium tetrachloride and nonvolatile uranium trichloride. Recovery of uranium is achieved by the reaction between uranium trichloride and fluorine at 250 to 500°C to produce volatile uranium hexafluoride which is collected in refrigerated traps. Both reactions are conducted in a fluidized bed of inert alumina particles.

Process studies are being conducted in a nickel apparatus consisting of a $1\frac{1}{2}$-in.-diameter fluid-bed reactor and a $1\frac{1}{2}$-in.-diameter packed-bed filter. Granular fused alumina has been found to be a satisfactory inert bed material under all process conditions. The packed-bed filter contains a bed of aluminum oxide particles and serves as a high-temperature filter for the retention of particulate solids entrained from the fluidized bed during the hydrochlorination reaction.

The primary aim of the process studies has been to establish conditions which would result in a minimal amount of unrecoverable uranium. Uranium losses are due primarily to: (1) passage of uranium through the packed-bed filter during the hydrochlorination step either as a volatile chloride species or as a particulate solid by entrainment in the gas stream, and (2) retention of uranium by the alumina in the fluid bed and filter bed at the end of the reaction sequence.

Generally, uranium losses through the packed-bed filter have been less than 0.2% of the uranium in the initial charge. A recent correlation of experimental data indicated[3] that the uranium loss through the packed-bed filter during hydrochlorination can be attributed to vaporization of uranium tetrachloride. The uranium loss is primarily dependent on the lowest temperature existing in the fluid-bed packed-bed system. The loss appears to be unaffected by the total mass of uranium in the initial charge, the rate at which the alloy is hydrochlorinated, and the quantity and particle size of the alumina on the packed-bed filter. It is concluded that, to minimize uranium losses, the unit should be operated at as low a temperature as possible, especially in the packed-bed filter section.

It has been demonstrated that the uranium loss in the fluid bed and filter bed can be reduced to about 1% of the uranium in the initial charge (corresponding to a uranium concentration in the bed material of 0.01 wt.%). Using a two-step fluorination procedure, 1 hr at 250°C followed by 2 hr at 500°C, workers achieved a residual uranium concentration of 0.007 wt.% in the bed material.[3] In both fluorination periods,

relatively high fluorine concentrations (50 to 90 vol.% in nitrogen) were used.

Infrared and mass spectrometric analyses of the contents of the uranium hexafluoride refrigeration traps indicated that about 7% of the chlorine initially associated with the uranium after hydrochlorination of the alloy is converted to chlorine trifluoride during fluorination.[3] In order to avoid the formation of chlorine trifluoride during fluorination, consideration is being given to treating the uranium chlorides with hydrogen fluoride prior to the introduction of fluorine.

Graphite-Matrix Fuels. Engineering-scale investigations on methods for processing graphite-reactor fuels are being conducted at Oak Ridge National Laboratory (ORNL).[4,5] These studies are applicable to the High-Temperature Gas-Cooled Reactor (HTGR) fuel or other reactor fuels containing uranium carbide in a graphite matrix. The initial step in the processing of graphite-matrix fuel is burning in oxygen to convert the graphite to volatile CO and CO_2 and to convert the uranium, thorium, and other materials to their respective oxides. The nonvolatile oxide ash is then treated by aqueous dissolution, fluoride volatility, or chloride-volatility methods.

Two methods of burning the fuel have been considered: (1) burning the fuel in a fluidized bed of inert particles such as alumina particles or (2) burning in a fixed bed of fuel. The first method is being extensively investigated at Brookhaven National Laboratory (BNL), and the fixed-bed burning concept is being developed at ORNL. The objective of the ORNL program is to develop engineering-scale equipment suitable for the recovery of uranium from irradiated uranium-graphite fuel.

A facility has been constructed for demonstrating the oxidation-fluorination process as shown in Fig. III-1. The burner is a 5-in.-diameter nickel pipe equipped with multiple-zone cooling facilities and several oxygen-injection ports. The fuel is supported within the burner on an alumina ceramic plate. Combustion gases are cooled prior to filtration through a bank of sintered metal filters. The carbon monoxide content of the off-gas is monitored continuously. It was difficult to maintain the CO concentration in the off-gas below the explosion limit; however, explosion hazards were minimized by off-gas dilution during periods of high CO evolution.

Burning rates as high as 4.0 gram moles of carbon per minute with wall heat fluxes of

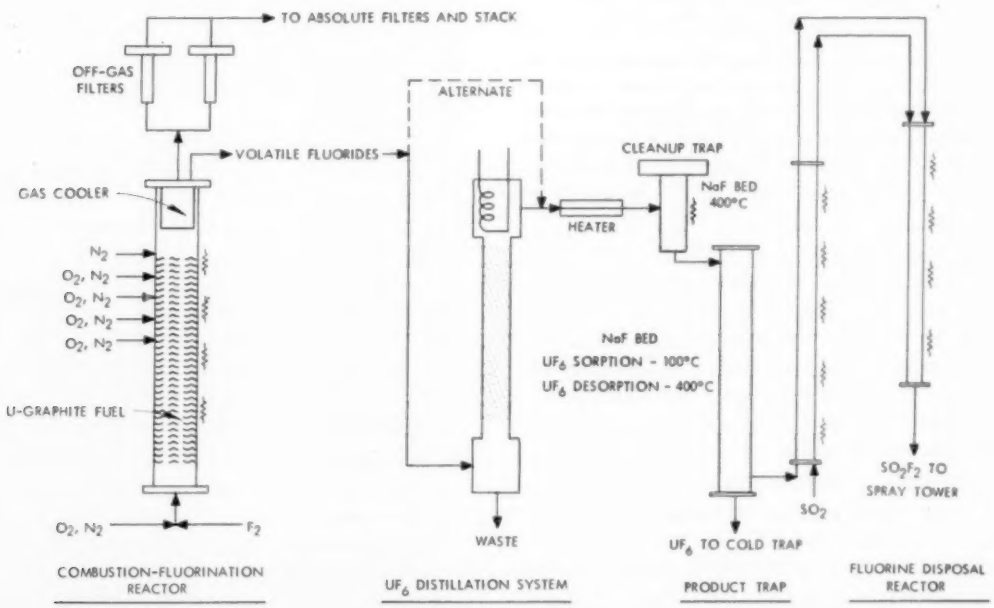

Fig. III-1 Combustion-volatility flow sheet for uranium-graphite fuels.[5]

40,000 Btu/(hr)(sq ft) were obtained without producing excessive sintering of the oxide ash. However, burner control at these high rates was difficult. Satisfactory conditions were found using 50 vol.% air–50 vol.% oxygen and reacting the fuel at a rate of 2.5 gram moles of carbon per minute. The uranium contained in solids collected on the sintered metal filters amounted to less than 0.2% of the uranium in the charge. The amount of uranium passing through the filters was less than 0.002%. Fluorination of the oxide ash, conducted at rates of 20 to 30 gram moles of fluorine per minute, resulted in the recovery of 98% of the uranium in the reactor. The utilization of the fluorine was about 50%.

Sintering of the oxide ash during burning, or the presence of large amounts of nonvolatile fluorides, hinders complete uranium recovery by fluorination owing to the formation of solid solutions and slow gas diffusion into the solids. In a small-scale combustion-fluorination experiment with HTGR fuel (carbon-coated ThC_2-UC_2 particles in graphite matrix: 21.1% thorium, 2.1% uranium, and 76.9% carbon), only 93% of the uranium was recovered in 45 min of fluorination at 420 to 520°C. The mottled appearance of the fluorination residue suggests that uranium was occluded in the thorium oxide. Complete uranium recovery may only be achieved after prolonged fluorination times.

Chloride-volatility processes are also being investigated on a laboratory scale as a means for treating graphite and carbide fuels. Investigations have proceeded on developing chloride-volatility processes either as an independent method or as a head-end step for aqueous dissolution or fluoride-volatility decontamination methods.

The more promising of the chloride-volatility processes studied involves high-temperature gas-phase chlorination of the oxide ash produced by burning the reactor fuel in oxygen. The combustion-chlorination volatility process involves five separate operations requiring a total time of about 9 hr as determined from laboratory-scale tests.

1. The fuel is burned in pure oxygen at 800°C.
2. The oxide residue is chlorinated with 15 vol.% CCl_4–85 vol.% Cl_2 at 500°C; this step completely converts the oxide residue to volatile chlorides.
3. The volatile chlorides are collected in a condenser maintained at 25°C.
4. The more volatile chlorides are removed from the uranium chloride by volatilization at 400°C in an inert-gas stream; uranium remains behind as uranium tetrachloride.
5. The uranium is recovered by either dissolution in nitric acid or by fluorination to volatile uranium hexafluoride.

As an alternative to step 4, uranium may be separated from associated chlorides by volatilization of the mixed chlorides through a bed of sodium chloride at 500°C. The uranium chlorides are completely retained on the bed, whereas most other volatile chlorides pass through the bed unaffected.

Both the burning and chlorination steps are conducted in a single vessel. Under the conditions recommended, laboratory corrosion tests have indicated that A-nickel experiences a corrosion rate as low as 1 mil/month. It appears that an oxide layer formed on the metal during burning protects the substrate during the chlorination period.

A direct chlorination head-end treatment has been studied for graphite-matrix fuels. The direct chlorination process involves the treatment of ground fuel at 800°C with a series of four chlorinating reagents. The total processing time has been estimated to be 9 hr. The process sequence involves:

1. Reaction of the ground fuel for 1 hr with phosgene ($COCl_2$) at 800°C to produce volatile chlorides of uranium and associated materials. Approximately 95% of the uranium is volatilized in this step.
2. Any uranium trapped in the graphite-carbide residue is recovered by burning the residue in 50 vol.% Cl_2–50 vol.% H_2O at 800°C for 6 hr. The uranium is converted to oxide during this treatment.
3. The uranium oxide is chlorinated to volatile UCl_5 and UCl_6 in a 1-hr treatment at 800°C with 15 vol.% CCl_4–85 vol.% $COCl_2$.
4. A further treatment for 2 hr at 800°C with 15 vol.% CCl_4–85 vol.% Cl_2 converts nearly all the remaining uranium to volatile chlorides.

Laboratory-scale tests have indicated that all but 0.1% of the uranium in the graphite fuel is converted to a volatile chloride by this direct chlorination process. Although satisfactory uranium recoveries from graphite-matrix fuels may be realized by the direct chlorination process, the concept does not appear practical at the present time, since studies have shown that

most metals experience catastrophic corrosion under the proposed processing conditions. A ceramic might be sufficiently corrosion resistant to be used as a reactor material.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

Several processes that involve separation methods based on the volatility of uranium hexafluoride are being developed for the processing of uranium dioxide reactor fuel elements. A fluid-bed fluoride-volatility process (Fig. III-2) is being developed at ANL[3,6,7] to recover uranium and plutonium from spent oxide fuel. In this process, uranium and plutonium dioxides are fluorinated with fluorine to produce volatile uranium and plutonium hexafluorides that are subsequently decontaminated and separated from one another. Workers at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium,[8,9] are developing a fluorination process for the recovery of uranium from UO_2 fuel based on the initial conversion of the oxide to uranium tetrafluoride prior to fluorination to UF_6 in order to minimize fluorine requirements. Preliminary studies have been made by Naumann[10–12] on a chloride-volatility process for uranium dioxide.

Direct Fluorination of Uranium Dioxide Fuel. In the development of the fluid-bed fluoride-volatility process for uranium dioxide fuels, current emphasis has been placed on the evaluation of a two-zone oxidation-fluorination scheme (Fig. III-2) as a means of improving the performance of fluidized-packed beds of uranium dioxide. In this scheme the lower (oxidation) zone of the reactor consists of a bed of declad uranium dioxide pellets with fused alumina grain filling the voids of the bed (fluidized-packed bed), and the upper (fluorination) zone consists of a fluidized bed of fused alumina grain. Passing an oxygen-nitrogen mixture through the lower zone causes U_3O_8 fines to be produced and transported to the upper fluidization zone where the fines are fluorinated to uranium hexafluoride.

Demonstration of the oxidation-fluorination process scheme has been carried out on an engineering scale in a 3-in.-diameter air-cooled reactor. In recent tests[3] a 12-in.-deep fluidized-packed bed of declad UO_2 pellets (8.8 kg of UO_2) was completely fluorinated under conditions which resulted in both high UF_6 production rates and high fluorine utilization efficiencies. The operating conditions and the results of the tests are presented in Table III-1. Nearly 90% of the UF_6 produced was collected in 8.2 hr of fluorination, corresponding to a production rate of 54 lb of UF_6/(hr)(sq ft) and a fluorine efficiency of 79%. A final cleanup period of 3.25 hr was used to complete the fluorination of the alumina bed. This operation was carried out with high fluorine concentration in the gas stream and with total off-gas recycle. From the results of this test, it appears that successful fluorination of UO_2 pellets can be achieved by operating under the following conditions:

Temperature of the fluorination zone at 500°C with the temperature gradient in the oxidation zone from 480°C at the top of the bed to 340°C at the bottom; gas flow to the oxidation zone of 1.0 scfm containing 8 vol.% oxygen in nitrogen; gas flow in the fluorination zone of 1.5 scfm containing 9 to 15

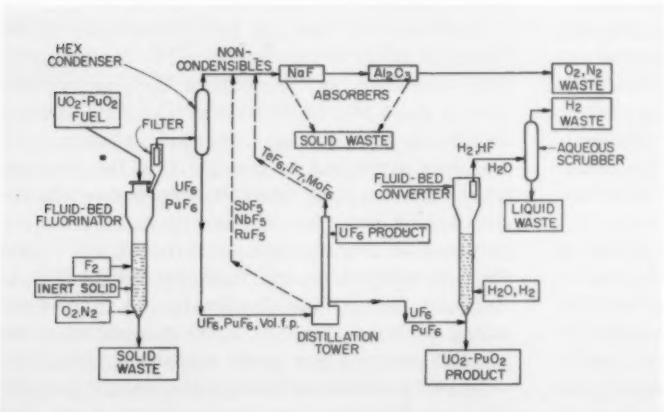

Fig. III-2 Conceptual flow sheet for a fluid-bed fluoride-volatility process.[6]

Table III-1 OPERATING CONDITIONS AND RESULTS FOR RUN UOF-70, A TWO-ZONE OXIDATION-FLUORINATION OF URANIUM DIOXIDE PELLETS WITH GAS PULSING[3]

UO_2 pellet charge:	Weight: 8.8 kg
	Bed height: 12 in.
Alumina charge:	Weight: 7.1 kg (Blue Label Alundum)
	Static height above pellets: 20 in.
	Size limits (U. S. Mesh): −40 +170
Temperatures:	Fluorination zone: 500°C
	Oxidation zone (pellets): 340 ≤ T ≤ 480°C
Pulsing conditions:	Duration: 0.04 sec
	Frequency: 2 pulses/min
	Pressure: 20 psig
	Gas volume: 0.016 cu ft/pulse
Oxygen diluent:	N_2
Fluorine diluent:	Process off-gas (0.25 cfm)
Run duration:	12.5 hr (9.25 hr once-through gas flow, 3.25 hr total off-gas recycle)
Overall fluorine efficiency: 75%	

Process time, hr	Gas flow: Oxidation zone Rate, cfm	Gas flow: Oxidation zone O_2, %	Gas flow: Fluorination zone Rate, cfm	Gas flow: Fluorination zone Average F_2 input to reactor, %	Average fluorine utilization efficiency,* %	Average production rate, lb UF_6/(hr)(sq ft)
0–3.5	1.04	8.0	1.44	10.2	69.4	37
3.5–8.5	1.04	8.0	1.51	14.4	85.8	68
8.5–9.25	1.04	8.0	1.42	9.4	46.4	23
9.25–12.5	(0.5-cfm gas recycle + 0.06 cfm F_2)				42.3	9

*Fluorine utilization efficiency = $100\left[\frac{3\ (\text{mole } UF_6 \text{ produced/hr})}{(\text{mole } F_2 \text{ fed/hr})}\right]$.

vol.% fluorine in nitrogen; gas pulsing with a small quantity of gas (0.016 cu ft/pulse, 2 pulses per minute) to aid in U_3O_8 fines transport from the oxidation zone to the fluorination zone.

Investigations are also being made[3] on the application of the two-zone technique for the processing of stainless-steel-clad pellets. Tests have been performed with short lengths (1 in.) of stainless-steel tubing simulating sheared fuel elements and with longer element sections which were perforated longitudinally with a series of slits. In two experiments carried out in the 3-in.-diameter fluid-bed reactor, removal of UO_2 from the stainless-steel tubing was complete with a 1.5-in.-deep fluidized-packed section and 95% complete with a 6-in.-deep packed section. These results were obtained in 8.5 and 13.5 hr, respectively.

Experimental work has been carried out at ANL[3] on the oxidation of uranium dioxide to U_3O_8 as a means of decladding chopped fuel elements in the fluoride-volatility process. The oxidation product forms as a very fine powder and readily separates from the cladding. Tests have been performed on the oxidation of 1-in.-long segments of ½-in.-diameter stainless-steel-clad UO_2 elements in a fluidized-packed bed. An optimum overall rate of removal of uranium from the cladding appeared to occur in oxidations carried out at temperatures between 400 and 500°C. By improved circulation of the inert fluid-bed material among the fuel segments and by imparting some movement to the segments, it has been possible to obtain complete separation of UO_2 from the cladding.

Experimental studies have been made on the fluorination of U_3O_8 fines in a 1½-in.-diameter fluid-bed reactor.[3] Powdered U_3O_8 is injected into a fluid bed of 120-mesh alumina with the fluidizing nitrogen gas stream. Fluorine (20 vol.% in nitrogen) is brought into the bed just above the point at which the powder enters the reactor. A reaction scheme employing two periods at a reaction temperature of 500°C has been developed: in the first period the U_3O_8 is fed into the bed, and fluorination is carried out using 20 vol.% fluorine in the gas phase; in the second period a gas phase containing 100% fluorine is recirculated through the bed for a period of 5 hr. With this reaction sequence, more than

99% of the U_3O_8 fed to the reactor was converted to UF_6. The reaction rate for the reaction of U_3O_8 with fluorine has been measured over the temperature range of 300 to 400°C. An average value of 30 kcal/mole was calculated for the activation energy of this reaction.

Volatility Processes Involving Pretreatment of UO_2 Fuel. Workers at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium, are developing a fluorination process for the recovery of uranium from sintered uranium dioxide fuel.[8,9] To minimize fluorine requirements, the oxide fuel is initially converted to uranium tetrafluoride prior to fluorination to UF_6 with fluorine. The sintered oxide is activated for hydrofluorination by an oxidation-reduction procedure. All reactions in the process, $UO_2 \rightarrow U_3O_8 \rightarrow UO_2 \rightarrow UF_4 \rightarrow UF_6$, have been studied in fluid-bed equipment. Oxidation of UO_2 pellets to U_3O_8 is carried out by reaction with 20 vol.% oxygen in nitrogen at 475°C. During the later stages of the reaction, the concentration of oxygen is increased to 60 vol.% in nitrogen.[9] It has been observed[8] in fluid-bed tests that UO_2, obtained by the reduction of U_3O_8 with NH_3 at 450 to 550°C, reacts more readily with hydrogen fluoride than UO_2 prepared under similar conditions by hydrogen reduction of U_3O_8. The UO_2 obtained by ammonia reduction has a higher specific surface than oxide prepared by hydrogen reduction of U_3O_8. Hydrofluorination of uranium dioxide is carried out at 500°C with 50 vol.% hydrogen fluoride in nitrogen. This reaction has been demonstrated in a fluid-bed reactor with a bed of aluminum oxide particles as an inert diluent.[8] It was observed that the uranium-bearing particles tended to agglomerate (cake) in the lower portion of the reactor, resulting in segregation of the uranium from the alumina particles. It is expected that this condition can be avoided through the use of high gas velocities during the reaction.

A modification of the process sequence has been suggested.[8,9] This modification involves the direct hydrofluorination of U_3O_8 to $2UO_2F_2$ and UF_4 and eliminates the reduction of U_3O_8 to UO_2. The reaction of U_3O_8 with HF has been studied in a fluid-bed reactor.[8] The problem of particle segregation within the fluid bed was less pronounced than in the case of hydrofluorination of uranium dioxide. The hydrofluorination of U_3O_8 is carried out with 50 vol.% HF in nitrogen in the temperature range of 300 to 500°C. Preliminary results of studies on iodine decontamination during the reaction between HF and U_3O_8 at 500°C indicate that nearly 100% of the iodine is eliminated from the oxide.[8] This decontamination level is significantly higher than that realized in the hydrofluorination of uranium dioxide.

An alternative approach for processing power-reactor fuels, being studied at CEN,[8,9] involves the oxidation of the fuel, or an intermediate compound, to uranium trioxide prior to fluorination with sulfur tetrafluoride to form uranium hexafluoride. Oxidation to uranium trioxide is achieved by reaction with nitric acid vapor at 340 to 400°C. The reaction temperature must be carefully regulated to avoid the formation of the gamma polymorph of uranium trioxide (gamma UO_3) which is considerably less reactive than epsilon UO_3. Gamma UO_3 is formed preferentially at temperatures below 340°C, whereas epsilon UO_3 is produced at temperatures above 340°C. Several tests[9] have been performed to evaluate nitrogen dioxide as an alternative oxidant to nitric acid vapor. The results of these studies indicated that NO_2 is not suitable since oxidation of UO_2 to UO_3 proceeded very slowly.

It has been observed[9] that epsilon UO_3 readily reacts with hydrogen fluoride at 200°C to form anhydrous uranyl fluoride. The activation energy of the reaction has been calculated to be 5.5 kcal/mole. It is proposed that this reaction be incorporated into the fuel-processing scheme, since it will result in a significant reduction in the quantity of sulfur tetrafluoride required to produce uranium hexafluoride.

Chloride Volatility. A method for processing irradiated uranium and uranium compounds based on the fractional sublimation of chlorides is being studied by Naumann.[10–14] Uranium dioxide fuels are chlorinated at 600°C with carbon tetrachloride (30 vol.% CCl_4 in CO_2) at 300 torrs.[11] The volatile chloride products are discharged directly into a bath of fused NaCl-KCl at 750°C. Uranium tetrachloride is completely removed from the gas stream by absorption into the melt. The decontamination of uranium was less than 45 from zirconium, niobium, and tellurium; was very low from ruthenium and cesium; and was 1180 from cerium. In tests made with samples of uranium dioxide containing 1000 ppm plutonium, it was observed that 60% of the plutonium accompanied the volatile

uranium chlorides and appeared in the chloride melt. This behavior of plutonium was not expected. Subsequent work[12] showed that a separation of plutonium from uranium can be achieved by gas chromatography of the plutonium chloride on activated carbon. The volatile chlorides are initially absorbed on the carbon at 600°C. After the carbon bed is flushed with inert gas at 700°C, the uranium is preferentially removed, effecting a distinct separation of plutonium from uranium.

Properties of Fluorides

Uranium Hexafluoride. Hayman and Stuart[15] have determined heat of formation of uranium hexafluoride by direct combination of the elements in a calorimeter. The derived thermochemical data at 25°C were: for UF_6 (gas), $\Delta H_f^\circ = -510.49 \pm 0.57$ kcal/mole, and for UF_6 (solid), $\Delta H_f^\circ = -522.36 \pm 0.57$ kcal/mole. These values are in complete agreement with those obtained by Settle et al.[16] and recently reported in *Reactor Fuel Processing*.[17]

The reactions of molybdenum hexafluoride, tungsten hexafluoride, and uranium hexafluoride with nitryl fluoride, nitrosyl fluoride, and nitrosyl chloride have been studied by Geichman, Smith, and Ogle.[18] The reactions of all three hexafluorides with nitrosyl fluoride and nitryl fluoride resulted in solid compounds of the composition $NO_XF \cdot MF_6$ where X is 1 or 2 and M is tungsten, molybdenum, or uranium. Nitrosyl chloride reduces molybdenum and uranium hexafluoride to produce complex nitrosyl fluorides of Mo(V) and U(V) with the liberation of chlorine. Tungsten hexafluoride does not react with nitrosyl chloride.

Trevorrow and associates[19] have studied the reaction between uranium hexafluoride and hydrogen sulfide at 25°C and have observed that the products of the reaction are uranium tetrafluoride, sulfur tetrafluoride, and hydrogen fluoride. In the same study it was found that uranium hexafluoride reacts with carbon disulfide vapor at 25°C to produce uranium tetrafluoride, sulfur tetrafluoride, bistrifluoromethyl disulfide $[(CF_3)_2S_2]$, and bistrifluoromethyl trisulfide. At elevated temperature the reaction also produces sulfur hexafluoride and tetrafluoromethane.

Decontamination of uranium hexafluoride, produced by fluoride-volatility techniques, can be accomplished by an absorption-desorption cycle in a bed of sodium fluoride pellets. Workers at ORNL[20,21] have investigated the removal of UF_6 from a gas stream by a single layer of sodium fluoride pellets. Experimental data on the rate and extent of sorption were obtained[20] in the temperature range of 29 to 100°C and with a UF_6 concentration range of 0.57 to 10.9 mole %. The results of the study indicate that the rate-controlling mechanisms are: transfer of UF_6 across a stagnant gas film surrounding the pellet, diffusion of gaseous UF_6 in the pores of the pellet, and diffusion of UF_6 through a layer of the UF_6–NaF complex covering the unreacted sodium fluoride in the interior of the pellet.

Katz[21] has observed that the composition of the complex formed between UF_6 and sodium fluoride is $2NaF \cdot UF_6$. The crystalline density of the complex was determined[20] to be 4.13 g/cm^3; this indicates that incomplete reaction of the sodium fluoride will occur for pellets in which the initial void volume fraction is less than 0.807.

The sorption characteristics of molybdenum and tungsten hexafluorides on sodium fluoride have been studied at ORNL.[22] Adsorption of MoF_6 on sodium fluoride was rapid in the temperature range of 160 to 182°C, whereas outside this range adsorption was considerably slower. In the range of high adsorption, a complex corresponding to $2.3\ NaF \cdot MoF_6$ was obtained. Adsorption of WF_6 on sodium fluoride was rapid at all temperatures above 190°C. The complex obtained in these cases was $2.3\ NaF \cdot WF_6$. The dissociation pressures of the hexafluorides over the complex compounds were:

$$MoF_6\text{-}NaF: \log P_{mm} = 8.44 - 2.94 \cdot 10^3/T$$

$$WF_6\text{-}NaF: \log P_{mm} = 7.10 - 3.13 \cdot 10^3/T$$

A process based on sorption-desorption from a bed of magnesium fluoride pellets is also being developed at ORNL for decontaminating uranium hexafluoride. A series of gasometric studies[22] has shown that the retention of uranium on magnesium fluoride is due to physical adsorption; uranium hexafluoride is reversibly adsorbed in quantities much smaller than normal for chemical complex formation. Technetium is readily adsorbed on magnesium fluoride, and two schemes for release of the physically adsorbed UF_6 and isolation from technetium are suggested. One scheme depends on the prefer-

ential desorption of the UF_6 at 300°C with an inert sweep gas. The alternative method depends on the selective adsorption of UF_6 by sodium fluoride pellets after both uranium and technetium are desorbed from the MgF_2 pellets with fluorine at 500°C.

Plutonium Fluorides. Deichman and Tananaev[23] have measured the solubility of plutonium tetrafluoride in sodium fluoride solutions and have observed that two compounds, $NaPuF_5$ and Na_2PuF_6, are formed.

Selective thermal decomposition of plutonium hexafluoride is being considered as a means of separating the mixture of uranium hexafluoride and plutonium hexafluoride produced in the fluorination of uranium dioxide fuel. It has been demonstrated[7] that circulation of gaseous mixtures of UF_6 and PuF_6 through nickel vessels containing nickel wool at temperatures of 200 to 300°C reduces the ratio of plutonium to uranium by factors between 10^2 and 10^3 as a result of decomposition of PuF_6 to PuF_4. The solid product remaining in the vessel is PuF_4 containing 0.09 to 1.3% uranium. It appears that thermal decomposition can be used to separate PuF_6 from UF_6 at rates that are practical for application to the fluoride-volatility process.

Steindler has published a complete review of the literature concerning the properties of plutonium hexafluoride.[24] Included in this survey are data on the preparation of PuF_6, physical properties, absorption spectra, chemical reactions, decomposition of PuF_6 by radiation and heat, and the corrosion of construction materials by PuF_6. Also included is a summary of the biological and radiological hazards from plutonium hexafluoride.

Reactions Involving Fluorine. Kelly, Post, and Mason have investigated the reaction between fluorine and alkali-metal halides at elevated pressures and temperatures.[25] It was observed that, at 300°C and a pressure of 3400 kg/cm^2, the reaction between fluorine and potassium chloride produces potassium tetrafluorochlorate ($KClF_4$) in 90% yield. Similar compounds are formed by fluorination of RbCl and CsCl. Attempts to form corresponding compounds by the interaction of fluorine with NaCl or LiCl at elevated pressures and temperatures were unsuccessful. Potassium tetrafluorochlorate is a very strong oxidizing agent which explodes on contact with water. The tetrafluorochlorates may be useful as fluorination agents or as a means for storing fluorine in the form of a solid compound.

Metallic copper is frequently used as a construction material in applications involving fluorine service. A study of the fluorination of massive copper by fluorine in the temperature range of 300 to 600°C has been reported.[26] The experiments were conducted in a nickel reactor. It was observed that both the rate of fluorination and the depth of copper fluoride film increased with rising temperature. X-ray studies and chemical analyses indicated that only one fluoride phase was formed, namely, copper difluoride. At 300°C the rate of fluorination was found to follow a logarithmic law, whereas at temperatures of 400°C and above, the fluorination rates can be expressed by a parabolic law. The activation energy for the fluorination of copper at temperatures above 300°C was calculated to be 17.9 kcal/mole.

Edwards and associates[27] have reported the preparation of technetium oxide tetrafluoride ($TcOF_4$) by direct fluorination of technetium metal. The other products of the reaction were TcF_5 and TcF_6. The source of oxygen in the preparation of $TcOF_4$ is not clear, but it has been observed that TcF_5 begins to decompose in glass at 60°C. $TcOF_4$ is a blue compound with a melting point of 134°C and is similar in physical properties to the rhenium analog.

(J. J. Barghusen)

Pyrometallurgical Processes

Pyrometallurgical processes are being developed in order to achieve rapid recycle of discharged fuel in as direct a manner as possible. Included in such processes are those in which metallic fuels are purified directly as metals and others in which metallic fuels and ceramic fuels are purified in liquid-metal and salt systems. The potential economic advantages of these processes lie in their ability to handle short-cooled fuels, which makes possible minimum fuel inventories, and in the avoidance or simplification of chemical conversions. Other advantages of these processes are the direct production of solid wastes, the absence of severe critical mass restrictions, and, in some processes, the retention of valuable fuel alloying additives.

EBR-II Fuel-Cycle Facility

The EBR-II Fuel-Cycle Facility[17] is a processing plant for recovery and purification of discharged EBR-II fuel material.[28] It is a flexible facility designed to accommodate several pyrometallurgical processes that are to be demonstrated in the course of its operation. Melt refining, the most completely developed pyrometallurgical process, will be initially employed for recovery of the first core loading* of the EBR-II. In the melt-refining process, the fuel is melted, held at 1400°C for several hours, and then poured to cast an ingot. Fission products are removed at the elevated temperatures of operation through volatilization and selective oxidation reactions. The facility includes rather elaborate equipment for dismantling the discharged fuel and for refabrication of the purified fuel material into new fuel elements for recycle to the reactor. Thus the EBR-II will operate on a closed fuel cycle and will be the first reactor in the U. S. power demonstration program to do so.[28]

Two melt-refining furnaces and two injection-casting furnaces (the furnaces in which new fuel pins are cast) have been installed in the facility and have been in operation for some time with unirradiated fuel. Ingot yields in the melt-refining runs[29] have ranged between 93 and 97%. In the injection-casting furnace, pins are cast to the proper diameter (0.144 ± 0.001 in.) by pressuring molten fuel into Vycor tube molds. In the latest injection-casting run, 90 out of a possible 91 full-length (in excess of 14 in.) castings were obtained.[30]

At the present time, other equipment is being installed in the facility and is being put into operating condition in preparation for processing the first discharged fuel material expected in mid-1964. Progress in equipment installation is reported in recent progress reports of ANL's reactor development program.[29–31]

Two major items of equipment are required for remote disassembly of fuel subassemblies: (1) a dismantler for disassembly of the core subassemblies, and (2) a decanning machine for removal of the stainless-steel cans and other stainless-steel hardware from the 0.144-in.-diameter 14-in.-long fuel pins and for breaking the fuel pins into short (about 1½ in.) lengths for processing. The dismantler and its supporting equipment are shown[29] in Fig. III-3. Figure III-4 shows a fuel element being removed from a subassembly by means of a model 8 master-slave manipulator. All cutting operations are chipless, and the cooling system utilizes suction flow to minimize the spread of contamination. An operational test of the cooling system has shown that about 4 kw of heat may be removed, 30% in excess of the design requirement of 3 kw, thus assuring that fuel-element temperatures will be kept below the design maximum[29] of 600°F. Individual components of the dismantler are easily removable for remote repair. In fact, the entire dismantler was installed remotely in the Air Cell[17] in about 10 days by operating personnel.

Two decanning machines (see Fig. III-5) have been delivered, one of which has been installed in the Argon Cell[17] of the Fuel-Cycle Facility, the other of which has been set up outside the cell for out-of-cell tests.[29] About 8 hr was required to set up the machine remotely after the individual parts had been transferred into the cell. The decanning operations are illustrated schematically in Figs. III-6 and III-7. About 150 unirradiated fuel elements (canned fuel pins) have been decanned within the Argon Cell, 40 of which were sodium bonded. Some difficulty was experienced in decanning the sodium-bonded pins because the sodium adhered to metal surfaces in the extremely dry (a few parts per million water) argon atmosphere. The sodium-bonding effects were more severe than had been experienced with an earlier version of the decanning machine which had been operated in an argon atmosphere containing 100 to 1000 ppm water.

The argon atmosphere in the 65,000-cu ft Argon Cell is continuously purified by circulating the argon at a rate of about 200 cfm through a purification system. Oxygen is removed by converting it to water which, together with water introduced directly into the cell gas, is removed in a Molecular Sieve dryer. The oxygen is converted to water by reacting it with hydrogen in a palladium catalyst bed. There are indications that the catalyst bed has been poisoned.[29,30] This will require that it be removed and replaced by a new catalyst bed. Tests will be made on the poisoned bed in an attempt to discover the poisoning agent. Despite the loss

*An enriched-uranium (nearly 50% U^{235})-fissium alloy. Fissium is a mixture of the relatively noble fission-product elements, such as molybdenum and ruthenium, which are used as alloying elements in the fuel.

of catalyst activity, it has been possible to maintain high purity of the argon gas (5 ppm oxygen and 2 ppm water) by operation of the cell at a pressure slightly above atmospheric to reduce inleakage of air. This indicates the absence of major sources of oxygen and water vapor within the Argon Cell.

At the present time, nitrogen is not removed from the argon atmosphere of the EBR-II Fuel-Cycle Facility. The equilibrium nitrogen concentration, which will depend on the rate of air inleakage and the input of high-purity argon to replace that lost in locks, is expected to be about 5 vol.%. The removal of nitrogen from argon by gettering the nitrogen on hot (900°C) titanium sponge is under study because of a possible future need to remove nitrogen from the argon atmosphere in the Argon Cell.[30] Construction of a 10-cfm pilot plant for obtaining information on component reliability is essentially complete.[30]

Melt-Refining Technology

In the melt-refining process to be used for recovery of the first EBR-II core loading, the reactive fission products, such as the rare earths and alkaline earths, react at the wetted crucible surfaces with oxygen provided by the zirconium oxide crucible and remain in a reaction layer along the crucible wall. Preparations have been made at ANL to investigate the recovery of uranium-plutonium-fissium fuels, which may be used in future EBR-II cores, by an alternative process performed beneath a molten halide salt layer.[29] As compared with the present melt-refining process, the alternative process has the advantages of higher yields and lower operating temperatures. The rare-earth elements are expected to be preferentially oxidized and extracted into the salt layer without significant loss of either uranium or plutonium. The melt-refining operation is conducted in an argon-atmosphere induction-heated fur-

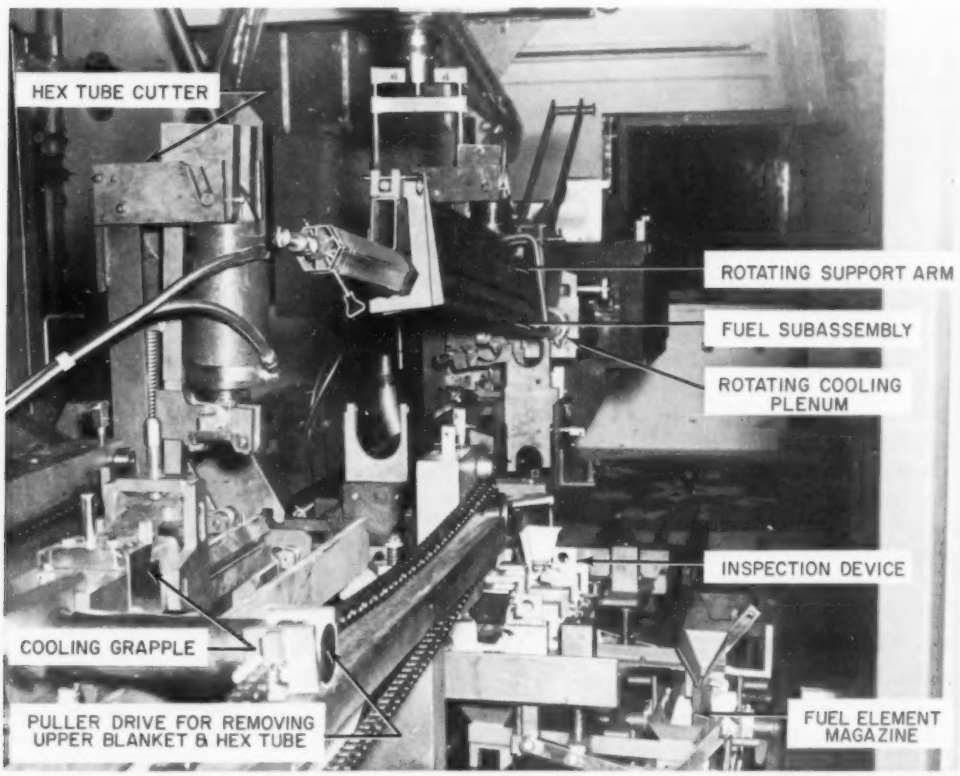

Fig. III-3 EBR-II core subassembly dismantler as installed in the Air Cell of the Fuel-Cycle Facility.[29] (A fuel subassembly is shown being rotated to the horizontal position.)

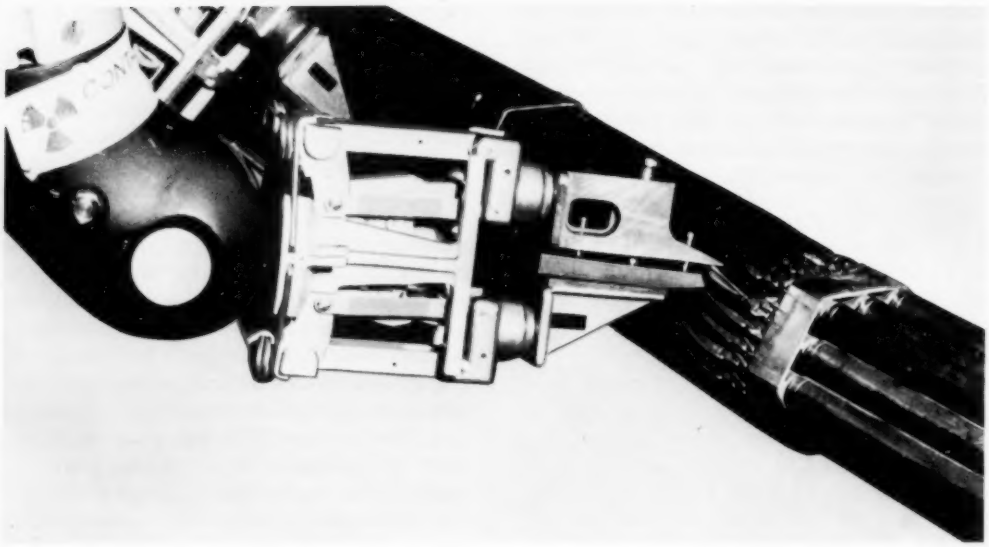

Fig. III-4 An attachment to the tong of the master-slave manipulator is being used to remove a fuel element from the grid support rail of a fuel subassembly.[28]

nace and is complete within 1 hr at 1150°C. Beryllia crucibles are used since they are not attacked by either the molten salt or uranium and are not wetted by molten uranium.

Preliminary experiments with uranium have shown the most satisfactory salt composition to consist of 75 mole % barium chloride and 25 mole % calcium chloride to which is added an amount of magnesium chloride 10% in excess of that required to oxidize rare-earth and alkaline-earth fission products. At the conclusion of the melt-refining operation, complete separation of the metal and salt phases has been obtained in a two-pour operation in which the uranium was first solidifed by cooling to 975°C, at which point the still-molten salt was poured off. The uranium was subsequently poured at 1300°C. Volatilization of the salt phase was negligible in these preliminary experiments.

Purification of Metals by Other Melting Techniques

French workers[32] have reported on the purification of uranium by floating zone refining (vertical zone melting), in which the zone was melted by electron bombardment. The degree of purification was determined by measuring the electrical resistivity of the uranium and qualitatively by observing whether secondary crystallization of the uranium occurred following heavy deformation of the uranium. This type of recrystallization has been observed only with high-purity uranium and does not occur in normal reactor grade uranium in which it is inhibited by impurities. The phenomenon of secondary recrystallization in high-purity uranium has been discussed by de Libanati, Calais, and Lacombe.[33]

The purification of beryllium[34,35] and aluminum[36] by zone refining has also been reported in recent articles.

Development of Liquid-Metal and Salt Processes

Liquid-metal and salt systems are frequently used as solvent media for processing reactor fuel materials and in the production of metals. Further work on the development of two liquid-metal and salt processes for the EBR-II fuel cycle (for the recovery of melt-refining residues and for the concentration of plutonium bred in the uranium blanket) is reported in recent progress reports of ANL.[29-31]

Workers at ANL are currently involved in the development of a countercurrent liquid-metal–salt extraction process for separation of uranium and plutonium from fission products. Separations are based on differences in

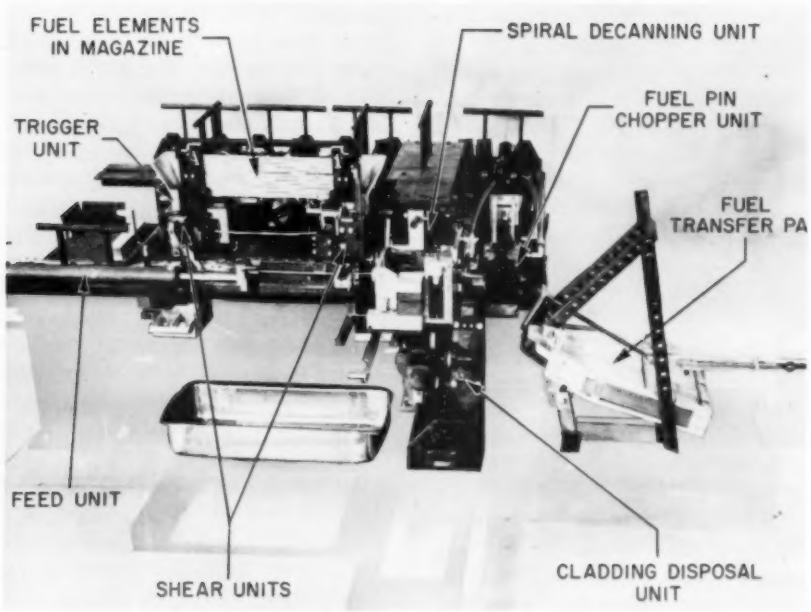

Fig. III-5 EBR-II fuel-decanning machine.[29]

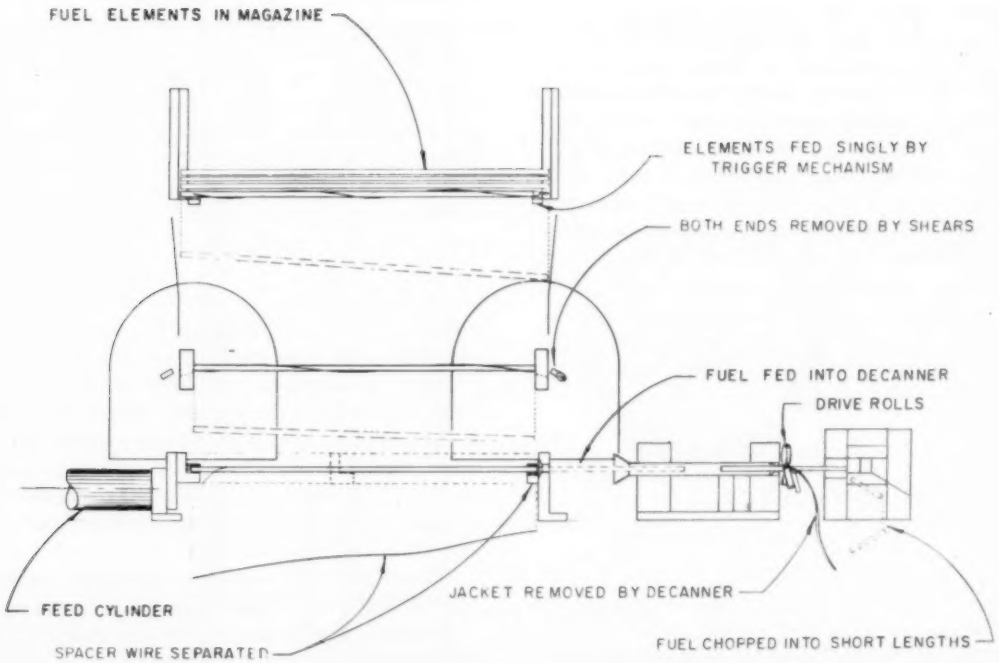

Fig. III-6 EBR-II fuel-decanning operations.[29]

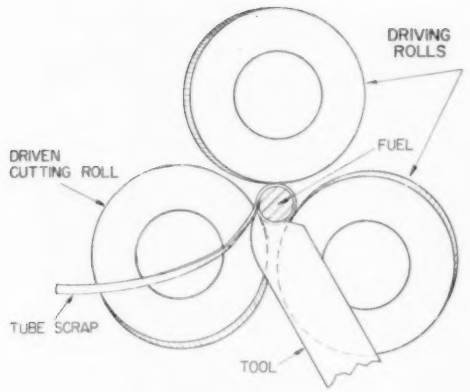

Fig. III-7 Detailed view of the rotary shearing operation used on the spiral decanner.[29] (The stainless-steel tubing is sheared into a spiral strip by the tool and the cutting roll.)

solute distribution behavior between liquid-metal and salt systems. Separation of fission-product, actinide, and transplutonium elements between magnesium-zinc metal and magnesium chloride salt systems were reported in a previous Review.[37] A ternary cadmium-magnesium-zinc system is currently being investigated as the metal phase. The ternary alloy solvent is less corrosive than the magnesium-zinc alloy and permits operation at lower temperatures (500 to 600°C instead of 800°C). Corrosion of 400-series stainless steels by the ternary alloy and salt systems composed of lithium, potassium, and magnesium chlorides is sufficiently low to allow use of these steels as construction materials.[31] Measurements of uranium solubility in the ternary alloy as functions of temperature and alloy concentration are currently being made. Uranium solubility increases with increasing zinc concentration and decreases with increasing magnesium concentration as shown below:[30]

Zn, at.%	Mg, at.%	Cd, at.%	Uranium solubility at 600°C, wt.%
		100	2.1
13	13	74	3
13	20	67	2.2
20	10	70	4.4*
20	13	67	3.5
20	20	60	2.7
100			0.2

*Measured at 650°C.

At 600°C the maximum observed uranium solubility was 3.8 wt.% (in cadmium–20 at.% zinc–10 at.% magnesium): at 700°C, uranium solubilities as large as 6 wt.% have been found in an alloy containing 30 wt.% zinc.[31]

The distribution of transplutonium elements between molten zinc-magnesium alloys and magnesium chloride has also been of interest because of the possibility of effecting transplutonium-element separations in these systems. Distribution data for americium and curium were previously reported.[37] Americium favored the salt phase, curium the metal phase. Distribution data have been obtained[30] for Cf^{252} between a liquid magnesium-zinc alloy and magnesium chloride. Unlike americium and curium, californium shows a variable behavior, strongly favoring the flux phase at magnesium concentrations below 20 wt.%, but showing an increasing tendency to distribute to the metal phase as the magnesium concentration was increased from 20 to 84 wt.%.

Chiotti has made a theoretical study of the separation of solutes by countercurrent extraction in a two-phase system wherein the transfer of the solutes between the phases is dependent on oxidation-reduction reactions of fixed stoichiometry.[38] The separation was shown to be analogous to separation of components in a distillation column, and the calculations were illustrated by the development of a flow diagram for separating two solutes, such as thorium and uranium, in a KCl-LiCl/zinc system. Mathematical relations and graphical methods for determining the number of equilibrium stages required to effect a given separation were presented by Chiotti.

Preparation of Metals by Reduction of Their Compounds

Reactive metals, such as thorium, uranium, and plutonium, are generally produced by electrolytic or chemical reduction of their halide salts, often from halide salt solutions. These reduction processes are closely related and are often involved in pyrometallurgical processes for reactor fuels. Pidgeon has recently discussed methods that are employed for the production of reactive metals.[39]

The following information has been published on the electrolytic production and purification of nuclear materials in molten-salt electrolytes:

1. In a review article,[40] Chauvin, Coriou, and Hure of France have summarized their work

and that of others on the use of electrorefining for the industrial-scale purification of commercial beryllium, plutonium, thorium, uranium, and titanium. Various factors that influenced the purity of the products were examined. The application of electrorefining to purification of irradiated nuclear fuels was discussed.

2. Molten fluoride salt electrolysis at 1200°C was investigated on a laboratory scale by Rafalski[41] of Poland as a means of producing uranium from uranium oxides. He also reported experiments on the electrolytic codeposition of thorium and zinc from molten fluoride baths at 1100°C.

3. Curtis of Hanford has reported[42] on the successful demonstration of continuous electrowinning of plutonium metal from plutonium trichloride maintained at a 30 wt.% concentration in a molten chloride bath which also contained 28 wt.% barium chloride and 40 wt.% potassium chloride. Plutonium was produced at a rate of 50 g/hr in runs of up to 10 hours' duration with a cathode efficiency of 60%. Continuous operation was effected by providing for underflow removal of the plutonium product. Nuclear safety was achieved by placing the entire system (see Fig. III-8) within a 57-mm envelope. Slip-cast ceramic oxide cells and induction heating were used to permit rapid attainment of an operating temperature of 800°C. The system was able to handle some plutonium oxide in the plutonium chloride bed. The purity of the product is limited by nonvolatile impurities in the feed. The impurities that form low-boiling chlorides are vaporized.

Patents were issued to Knighton[43] for a process for reducing an actinide oxide to metal by reducing the oxide suspended in a molten chloride flux with a magnesium-zinc alloy, and to Teitel[44] for reduction of uranium oxides with molten magnesium, after which the magnesium is filtered off. The residue from the latter process is heated with aluminum to form a uranium-aluminum alloy, which is removed through a filter to effect a separation from magnesium oxide.

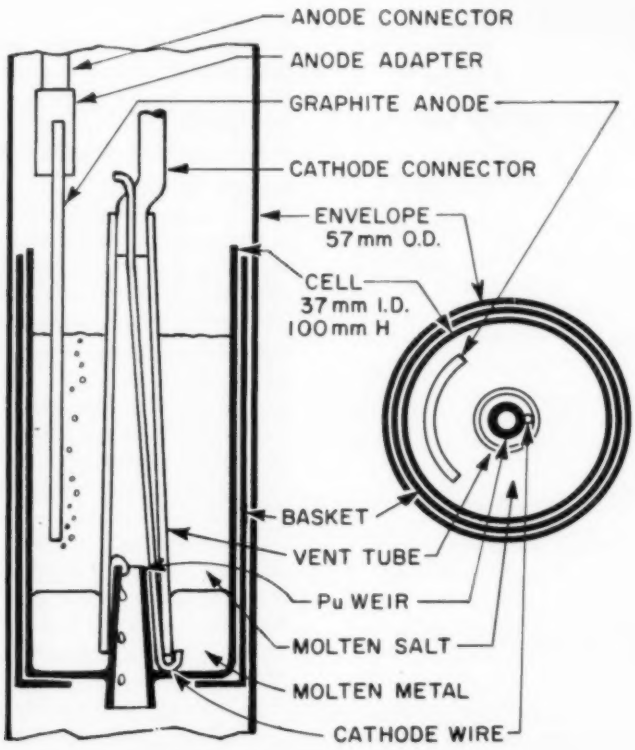

Fig. III-8 Plutonium electrowinning cell.[42]

Fundamental Studies Relative to Liquid-Metal Process Development

The logical design of pyrometallurgical processes requires the accumulation of considerable fundamental information on the chemistry of liquid-metal and salt systems.

Thermodynamic Data

In the preceding Review,[17] information was presented on the solubility of plutonium in cadmium. Revised equations have been presented[30] for calculating the solubility of plutonium in cadmium as a function of temperature. The thermodynamics of the plutonium-cadmium system have been further studied in two galvanic cells.[29] The electromotive-force data show a peritectic transformation of $PuCd_{11}$ to $PuCd_6$ to occur at 402°C. This is in excellent agreement with the solubility studies, which placed the peritectic transformation at 404°C. Thermodynamic functions of rare-earth-metal–cadmium systems are also being evaluated by means of a galvanic cell, and data have been reported for the praseodymium-cadmium system.[30]

The solubilities of titanium and cobalt in mercury are being determined by Weeks and Fink at Brookhaven.[45] Over the temperature range of 500 to 700°C, the solubility of titanium increased from 4 to about 2000 ppm, and in the range 502 to 650°C it may be represented approximately by the relation:

$$\log (\text{ppm Ti}) = 12.30 - (9210/T, \text{°K})$$

The solubility of cobalt in mercury is <0.3 ppm at temperatures up to 650°C.

The utility of solubility data is increased by knowledge of phase-diagram relations. Further work has been reported from ANL on the yttrium-zinc system.[30] Ames investigators have published an article[46] on this system, which was described from other reports in a preceding Review.[47] The yttrium-plutonium system is being studied, along with other plutonium alloy systems, at Mound Laboratory[48] as a potential high-temperature reactor fuel alloy because of evidence that plutonium forms a solid solution with yttrium up to plutonium concentrations of between 18 and 22.5 at.% plutonium. Novotny and Smith[49] have recently reported on the thermodynamic functions for the formation of $ThMg_2$.

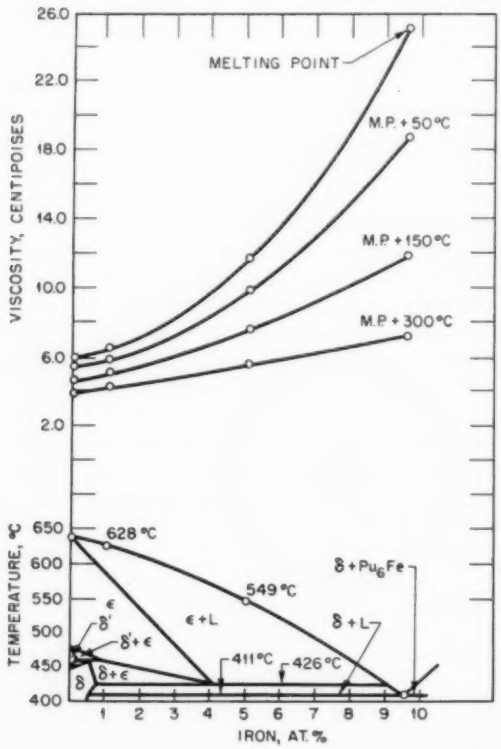

Fig. III-9 Viscosities of plutonium-iron molten alloys as a function of iron concentration and superheating temperature.[48]

Physical Property Data

Physical and thermal properties of fuel systems, particularly plutonium-bearing systems, are being determined at Mound Laboratory. The viscosities of a series of liquid plutonium-iron and plutonium-cerium-cobalt alloys have recently been reported[48] as a function of temperature (see Figs. III-9 and III-10). Mound Laboratory has also reported that the density of molten praseodymium decreased from 6.61 to 6.52 over the temperature range of 937 to 1190°C.

A differential thermal analysis apparatus (DTA) is being employed at Mound Laboratory to measure the vapor pressure of liquid metals by determining the boiling point at various system pressures.[48] Vapor pressures obtained by this method for cadmium and zinc have agreed well with literature values.

Stephens[50] has studied the effect of pressure up to 35 kbars on the phase transitions of plutonium, including melting. Spriet[51] of France

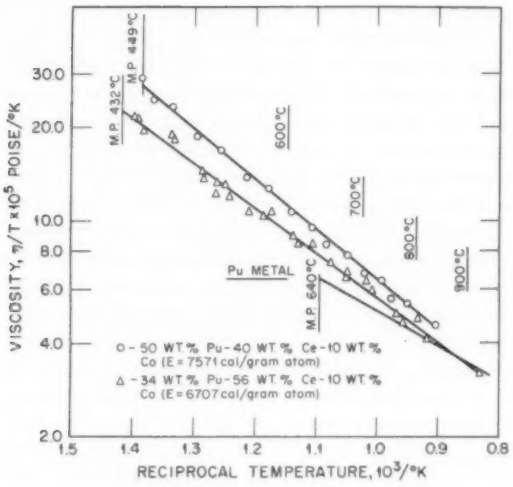

Fig. III-10 Viscosities of plutonium-cerium-cobalt molten alloys as a function of temperature.[48]

has determined in a floating zone-refining apparatus the surface tensions of uranium and plutonium at their melting points by the drop-weight method with results as follows: uranium, 1500 dynes/cm; plutonium, 550 dynes/cm.

Construction Materials for Liquid-Metal Fuel or Process Systems

A major objective of the Los Alamos Molten-Plutonium Reactor Experiments (LAMPRE) is the evaluation of combinations of plutonium fuel alloys and container materials in a reactor environment. At the present time the LAMPRE-I reactor is being operated with a plutonium–10 at.% iron alloy contained in tantalum-base capsules. Considerable work is also being done on other low-melting plutonium alloy systems, particularly plutonium-cerium-cobalt alloys.

Further evaluation of LAMPRE core II capsules (tantalum containing the plutonium-iron alloy) showed that intergranular penetration in the weld region had occurred in approximately 80% of the capsules.[52] These capsules had been removed after 988 Mw-hr of operation of LAMPRE-I.

Further out-of-pile corrosion testing of tantalum for containing the plutonium-iron alloy has shown double-arc-melted tantalum to be definitely superior to electron-beam-melted tantalum, especially at temperatures above 600°C. Initial tests show that an internal carbide coating is beneficial in protecting the tantalum container from intergranular penetration.[52]

Tests are continuing on the corrosion of tantalum at 600 to 700°C by plutonium-cobalt-cerium fuels[52] containing between 5 and 8 g of plutonium/cm^3. A reaction layer forms on the tantalum and consists of two distinct zones: (1) one near the tantalum surface, which is a diffusion layer consisting predominantly of tantalum and cerium dissolved in tantalum and (2) an outer layer which consists entirely of tantalum and cobalt and which appears to result from precipitation of these elements either during the test or upon cooling from the test temperature.

General Publications in the Liquid-Metal Field

The following general publications on liquid metals have appeared recently: (1) the fourth in a series of high-temperature liquid-metal technology reports issued by BNL[53] and (2) a report by DiStefano and Hoffman[54] on the corrosion mechanisms which appear to be operative in liquid alkali-metal–solid-metal container systems, with special emphasis on the refractory metals, niobium, tantalum, molybdenum, and tungsten. (L. Burris)

Other Nonaqueous Processes

Processes employing dry, high-temperature chemical conversions are being developed for oxide and carbide reactor fuels. Gases, molten salts, and liquid metals are generally utilized as reagents and process media. Because of the resistance of these materials to irradiation damage, processes of this type are well suited to closed, low-decontamination, remotely operated cycles for short-cooled high-burnup fuels.

Oxide Fuel Processing

Development work has continued at Hanford on the salt-cycle process, a closed-cycle process for the recovery of uranium dioxide–plutonium dioxide fuel associated with the Plutonium Recycle Test Reactor (PRTR).[55–58] The process involves the following steps: (1) mechanical decladding, (2) oxidation of the fuel to form a mixture of uranosic oxide (U_3O_8) and plutonium dioxide, (3) dissolution of the uranosic oxide–plutonium dioxide mixture in molten

LiCl-KCl by sparging the melt with chlorine and hydrogen chloride, (4) precipitation and recovery of plutonium dioxide by sparging the melt with chlorine-oxygen mixtures, (5) electrodeposition of uranium dioxide, either as a by-product or containing codeposited plutonium dioxide, and (6) electrode stripping, crushing, washing, and sizing of the uranium dioxide.

Engineering development of the process is being carried out on a scale of one-quarter of a PRTR fuel subassembly, or about 25 lb of uranium dioxide, per batch. Unirradiated Zircaloy-clad uranium dioxide fuel rods have been declad by bisecting the cladding with a tubing cutter and then removing the uranium dioxide by moving a vibrating air hammer along the inverted tube sections. Satisfactory recoveries were demonstrated with both cold-swaged and hot-swaged fuel rods.[58] Approximately 25 lb of uranium dioxide that had been declad in this manner was oxidized at 400°C by exposure to air at a rate of 2 liters/min for a period of 19 hr (Ref. 56). The resulting uranosic oxide was dissolved in a 70-lb bath of molten equimolar LiCl-KCl at 600°C by sparging the system with 50 vol.% chlorine–50 vol.% hydrogen chloride at 4 liters/min for 72 hr. A 24-lb batch of uranium dioxide was then electrodeposited on a pyrolytic graphite-coated cathode, using a potential of 1.4 volts and a gas sparge of 50 vol.% oxygen–50 vol.% chlorine over a 22-hr period. The uranium dioxide product was cut into $\frac{1}{2}$-in. cubes, washed with water to remove chloride impurities, dried, crushed, and screened to the proper size for refabrication by vibratory compaction.

A similar demonstration was conducted in which about 32 lb of uranium dioxide containing 58 g of plutonium was declad, oxidized, and introduced into a 65-lb equimolar LiCl-KCl bath.[57] Sparging with a gas stream composed of 1.5 liters of chlorine per minute and 1.5 liters of hydrogen chloride per minute resulted in dissolution of 90% of the uranium, but none of the plutonium after 24 hr. Upon further sparging, nearly all the uranium, but only 64% of the plutonium, was dissolved. It is considered likely that elimination of moisture in the process cell and reduction of air leakage into the salt vessel would be beneficial in keeping the plutonium in solution.

Laboratory studies of the salt-cycle process flow sheet have been carried out to determine the important process variables in the electrodeposition of uranium and plutonium oxides from the molten-salt solutions.[57] The indications are that, by using low current densities and a low oxygen-to-chlorine ratio in the sparge gas during the electrolysis, a rare-earth decontamination factor of 30 and a plutonium enrichment factor of 50 can be achieved.

Although uranium dioxide containing less than 5 ppm chloride can be readily prepared by electrodeposition under typical laboratory conditions, chloride contamination amounting to 100 to 200 ppm was encountered in the pilot-plant equipment.[55] It was found that small amounts of aluminum, molybdenum, and niobium, and probably other metals, act as carriers of chloride to the cathode deposit. It is suspected that these metallic impurities form oxychlorides, which are codeposited with the uranium dioxide. The presence of plutonium in the system appears to have no effect on the chloride content of the product. In the pilot plant, corrosion products from Hastelloy C, which is used in the cover of the molten-salt vessel, were shown to produce a high chloride content in the uranium dioxide product.

Reactions of Uranium Oxides in Molten Chloride Media

Further experimental work has been reported on the thermodynamic properties of the reaction

$$UO_2 + Cl_2 = UO_2Cl_2 \qquad (1)$$

in molten-salt solutions.[55–59] Chronopotentiometric and electrode impedance measurements have indicated that the electrolytic reduction of uranyl(VI) chloride to uranium dioxide proceeds by two reactions, each involving a one-electron transfer:

$$UO_2^{2+} + e^- = UO_2^+ \qquad (2)$$

$$UO_2^+ + e^- = UO_2(s) \qquad (3)$$

The shapes of the chronopotentiometric reduction curves were also typical of reduction to form a solid product, i.e., uranium dioxide. Additional confirmation of this mechanism was provided by a demonstration that the reaction

$$UO_2^{2+} + UO_2(s) = 2UO_2^+ \qquad (4)$$

takes place,[59] and by spectrophotometric evidence for the existence of uranyl(V) species in solution.[60] Although the precision of the electrochemical measurements was good, uncertain-

ties in the accuracy were considered to be such that conclusions concerning the activity of uranyl(VI) chloride in molten-salt solution were not made.[55] However, a nearly constant ΔS value for reaction 1 in NaCl-KCl and LiCl-KCl melts of varying composition suggests that the same uranyl(VI) species exists in the various melts. Additional evidence indicates that at least two uranyl(VI) species exist in LiCl-NaCl melts and that a third species is present in other molten chloride solvents. A strong dependence of the electromotive force of reaction 1 on the melt composition has been observed. For examination of the effect of this variable in a simpler, better understood reaction, electromotive-force melt composition curves have been determined for the reaction

$$Ni + Cl_2 = NiCl_2 \qquad (5)$$

in NaCl-KCl melts. As with reaction 1, the electromotive force increased linearly with increasing KCl:NaCl ratio, but with a smaller slope, implying less dependence of the electromotive force on the chloride "activity."

Spectrophotometric studies of reaction 4 in LiCl-KCl eutectic (59 mole % LiCl) have given equilibrium constants of 0.0016 at 500°C and 0.0050 at 600°C, where the concentrations are expressed in molarity and the solid uranium dioxide is taken at unit activity.[57] The measurements were made by reducing uranyl(VI) chloride at an initial concentration of 0.017M with hydrogen until solid uranium dioxide was present, then allowing the system to come to equilibrium. The uranyl(V) concentration was determined from its absorbance at the 1534 mμ peak (molar absorptivity = 25 at 500°C and 19.5 at 600°C). The uranyl(VI) concentration was determined in the range of 470 to 490 mμ. During the course of the measurements, it was established that the solubility of uranium dioxide in the molten salt is very low ($<2 \times 10^{-4}M$).

Gaseous Low-Decontamination Process for Uranium Dioxide

Effort is continuing at Atomics International[61–63] on the development of the gaseous oxidation-reduction (AIROX) process for uranium dioxide reactor fuels. The fuel cycle, which is operated remotely, involves decladding and comminution of the fuel by alternate oxidation with air or dilute oxygen at 200 to 600°C, and reduction with hydrogen at 600°C. The powdered uranium dioxide product is reenriched by blending and is then refabricated by cold pressing and sintering.

Fuel pellets that were previously processed and refabricated from irradiated uranium dioxide (5700 to 15,000 Mwd/metric ton) by the AIROX process are undergoing reirradiation in the Materials Testing Reactor (MTR). It is expected that the irradiation will be completed and that postirradiation examinations will be started by mid-1964 (Ref. 63).

Further engineering development of equipment for the AIROX process has been reported.[63] Provisions for processing and repelletizing uranium dioxide in the same facility are being made, a mockup of a sieve shaker has been completed, and a new sintering furnace has been designed.

Additional decladding experiments have been performed on uranium dioxide pellets contained in 20-mil Zircaloy tubing. The fuel rods, which were $\frac{1}{2}$ in. in diameter and 4 to 8 in. long, were punctured at 1-in. intervals and heated at various temperatures in oxygen at 1 atm pressure. At a temperature of 520°C, the cladding oxidized and broke into pieces; at 485°C it was oxidized but remained mostly intact; and at 460°C it split, and the oxidized uranium dioxide was successfully removed. Decladding of another specimen at 425°C was 90% complete in $3\frac{1}{2}$ hr. The results showed that temperature has a strong effect on the decladding operation.

Oxidation of Uranium Dioxide and Plutonium Dioxide

Some additional studies have been made recently of the oxidation of uranium dioxide, a reaction that is utilized in a number of different fuel-processing schemes. In one such study, thermogravimetric measurements were made on various uranium dioxide preparations which were oxidized in air at temperatures[64] up to 800°C. With linearly increasing temperature, finely divided uranium dioxide underwent oxidation by a two-step process in which a tetragonal phase of composition $UO_{2.35\pm0.02}$ was formed first, followed by conversion of this "U_3O_7" phase to uranosic oxide:

$$3UO_2 + \tfrac{1}{2}O_2 = U_3O_7 \qquad (6)$$

$$U_3O_7 + \tfrac{1}{2}O_2 = U_3O_8 \qquad (7)$$

This two-step reaction was characteristic of uranium dioxide having a surface area greater than about 1 m^2/g. The initial oxidation under

these conditions was observed at temperatures as low as 74°C and appeared to be complete at about 310 to 340°C. An activation energy of 19.1 kcal/mole was derived for reaction 6. The second reaction occurred at higher temperatures and was complete at 500°C. The rate of reaction 7 was about four times that of reaction 6. However, attempts to determine a meaningful activation energy of reaction 7 were unsuccessful because of the complexity of the reaction.

With low-surface-area uranium dioxide (<0.05 m^2/g), the overall reaction appeared to proceed in a single step in the temperature range of about 300 to 500°C.

In a study employing differential thermal analysis techniques, exothermal peaks for reactions 6 and 7 were obtained.[65] Reaction 6, a diffusion-controlled process, was observed at 210°C. Reaction 7 was characterized as a process involving nucleation and rupture of the powder grains. By calibration of the apparatus, it was possible to confirm existing data on the heats of reaction.

Some work has also been reported by Jackson and Rand[66] on the oxidation behavior of plutonium dioxide and its solid solutions with thorium dioxide, yttrium oxide, and uranium dioxide. It was established that the apparent hyperstoichiometry of plutonium dioxide previously reported resulted from surface adsorption of oxygen rather than from incorporation of interstitial oxygen ions into the crystal lattice. This behavior contrasts with that of uranium dioxide, for which nonstoichiometric compositions are well known. In the oxidation of uranium dioxide–plutonium dioxide solid solutions, only the uranium dioxide underwent oxidation. It was concluded that the inability of plutonium dioxide to oxidize further, even when a means for entry of the oxygen into the lattice is provided, results from the difficulty of forming the appropriate plutonium valence state.

Carbide Fuel Processing

Development of processes for the recovery of uranium monocarbide reactor fuels has continued at Atomics International.[61–63] In one process the uranium carbide fuel is oxidized at low temperatures (400 to 500°C) by air or oxygen, and the resulting uranium oxide is reconverted to the carbide by carbothermic reduction at temperatures of 1300°C or higher. The second process entails nitridation of the carbide by reaction with nitrogen at about 900°C to form a mixture of uranium nitride and carbon. Uranium monocarbide is regenerated from this mixture by heating it in vacuum at temperatures above 1500°C. The third process consists of electrolytic dissolution of the carbide in a molten chloride bath with deposition of metallic uranium on a molybdenum cathode. The metallic uranium deposit is dissolved in hot mercury and is reconverted to uranium monocarbide by distilling off the mercury in a hydrocarbon atmosphere. Of the three processes, the main emphasis is being placed on the oxidation-carbothermic reduction cycle.

Processing by the Carbide-Oxide-Carbide Cycle

The oxidation of uranium monocarbide prepared from uranium dioxide containing 2.5 to 10.0 wt.% fissia* is being investigated further to ascertain the effects of fission-product elements in irradiated carbide fuels.[61,62] In a series of oxidation experiments, nonirradiated uranium monocarbide containing the "fissium carbide" (carbides of fission-product elements) was exposed to air saturated with moisture for various periods of time, then placed in 200 mm of oxygen pressure in a thermobalance in order to measure its oxidation rate. The results summarized in Table III-2 are, in general, similar to those obtained with uranium carbide alone. The freshly melted material was relatively unreactive, whereas increasing oxidation rates were found for the material with increased exposure to moist air. In most cases the carbide was "reactive" after three or four days of exposure to moisture and ignited at about 250°C. After ignition, a sustained reaction occurred, which resulted in nearly complete conversion of the carbide to oxide.

The oxidation of uranium carbide is also being investigated on a kilogram scale in a controlled-atmosphere rotary furnace. Additional runs have been completed, using 2.25 and 5 kg of uranium carbide in the charge.[62,63] The runs were initiated with $\frac{1}{4}$ atm of air in the furnace, and the pressure was gradually increased to 1 atm. The 2.25-kg run was completed after $6\frac{1}{2}$ hr (240 to 550°C in 5 hr, $1\frac{1}{2}$ hr at 550°C), and the 5-kg run was essentially complete after $5\frac{1}{2}$ hr at 250 to 540°C with an

*The term "fissia" refers to a synthetic mixture of oxides corresponding approximately in composition to the fission-product oxides in irradiated uranium dioxide fuel.

average air flow rate of 35 to 40 scfh. In the latter run, additional finishing operations were carried out for 1½ hr at 550°C. During the oxidation, much of the heat was supplied by the exothermic reaction. Additional heat was supplied by clamshell heaters that were designed to open automatically when the temperature became excessive, thereby controlling the reaction rate. The utilization of oxygen in the air flowing through the furnace (at ~0.01 ft/sec) approached 100%. A comparison of the products from these two runs and from a previous run using 1 kg of uranium carbide[17] is given in Table III-3. The results indicate that a fairly uniform product was obtained from run to run and that nearly all of the product (the −200 +400 and −400 mesh fractions) was suitable as a feed material for subsequent reconversion to uranium monocarbide.

It has been found that uranosic oxide prepared by air oxidation of uranium monocarbide at 550°C contains carbonate, with typical values ranging from 0.42 to 0.78 wt.% carbonate, equivalent to 0.06 to 0.11 mole of carbon per mole of uranosic oxide.[61] Although it is suspected that, under the carbothermic reduction conditions (vacuum and a temperature of about 1000°C), the carbonate would be removed as carbon dioxide and would not enter into the reduction reaction, this point has not yet been completely resolved.

The grain-growth characteristics of uranium monocarbide pellets during annealing under vacuum and in argon have been investigated.[61,62] The vacuum treatment proved to be much more effective than the treatment in argon in increasing the grain size. In 24 hr of annealing under vacuum at 1750°C, the mean grain size in-

Table III-2 OXIDATION RATES OF SIMULATED RECYCLE URANIUM CARBIDE AS A FUNCTION OF ACTIVATION[62]

(Atmosphere: 200 mm Oxygen)

Fissia,* %	Carbon, wt.%	Oxidation rate† after activation for number of days indicated						
		1	2	3	4	5	6	7
2.5	4.30	4.4	6.8			10.7	11.8	
7.5	3.97	5.0	3.3			5.2		
2.5	4.70	4.8			8.2		9.7	
5.0	4.75	4.6	8.9	8.5				11.1
7.5	5.05	5.8	8.2	7.2	10.3			
10.0	4.96	4.2	4.3	6.7			7.3	

*In uranium oxide from which the uranium carbide was prepared.
†Weight gain in mg/(min)(g).

Table III-3 AIR OXIDATION OF URANIUM MONOCARBIDE IN ROTARY FURNACE[62,63]

UC charge, kg	Product U_3O_8 powder						
	Fraction, mesh size	Wt.% in fraction	Bulk density, g/cm³ Loose	Bulk density, g/cm³ Tap	Total carbon, wt.%	Carbonate, wt.%	Iron, ppm
1.02	+50	0.2	1.6	2.5	0.17	0.78	260
	−50 +200	2.0					
	−200 +400	9.7					
	−400	88.1					
2.25	+50	0.1	1.3	2.4	0.19	0.89	150
	−50 +200	1.1					
	−200 +400	6.7					
	−400	92.1					
5.0	+50	0.26					
	−50 +200	1.39	1.98	2.49	0.29	0.91	407
	−200 +400	23.73	1.51	2.86	0.18	0.93	106
	−400	74.62	1.26	2.42	0.18	0.97	100

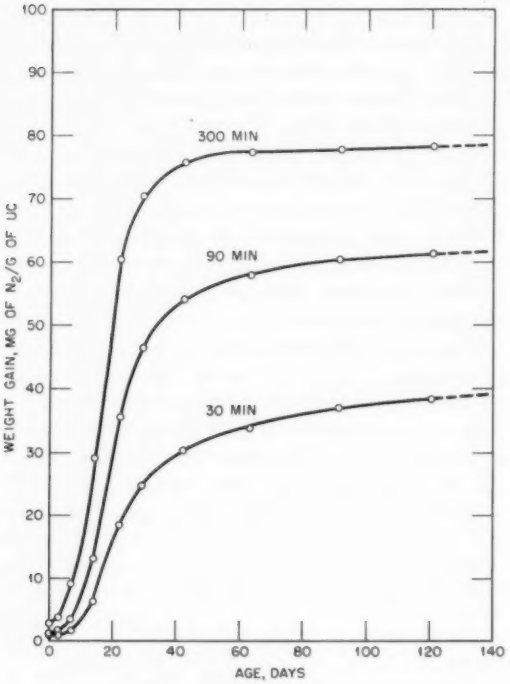

Fig. III-11 Reaction of UC with N_2 (N_2 weight gain vs. UC age).[67]

creased from 10 to 30 μ at the center of the pellets and from 10 to 70 μ at the outside of the pellets. Heating under hydrogen at 1700°C for 24 hr produced little grain growth but increased the pycnometer density from 11.5 to 11.8 and decreased the carbon content from 4.7 to 4.5 wt.%.

In the preparation of uranium monocarbide for vibratory compaction, the density of sintered uranium monocarbide agglomerates from previous experiments was much improved by crushing, presumably by opening up sealed voids.[63] Measurements on uranium carbide prepared from pressed uranium oxide–carbon pellets showed a similar effect. Although densities corresponding to 92% of theoretical are being obtained, somewhat higher densities would be desirable for vibratory compaction.

Processing by the Carbide-Nitride-Carbide Cycle

In connection with the carbide-nitride-carbide cycle for uranium carbide fuels, a report has been issued which deals with the kinetics of the nitridation reaction.[67] The effects of uranium carbide age, composition, and particle size and the influence of nitrogen pressure and temperature on the reaction rate were investigated. The measurements were made with a recording thermobalance, and the material used in the study was skull-cast uranium monocarbide. This material was arc melted to form buttons which were then crushed and screened. The uranium carbide was activated by varying periods of exposure to air saturated with water vapor at 22°C.

The product of the nitridation reaction was a grayish-colored powder. Combined samples from several experiments in which the reaction was more than 80% complete had approximately the following particle-size distribution:

Mesh	Wt.%
−50 +100	10
−100 +200	50
+200 −400	30
−400	10

X-ray diffraction results showed carbon and uranium sesquinitride to be the major reaction products, with traces of uranium dinitride as the reaction approached completion. In some samples from reactions at 850°C and above, uranium mononitride was detected.

The effect of age (period of exposure to moist air) of the uranium carbide on the reaction rate is illustrated in Fig. III-11. The greatest effect

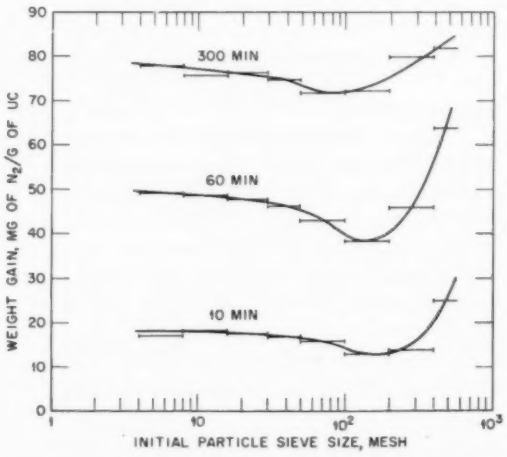

Fig. III-12 Reaction of UC with N_2 (N_2 weight gain vs. initial UC particle sieve size).[67]

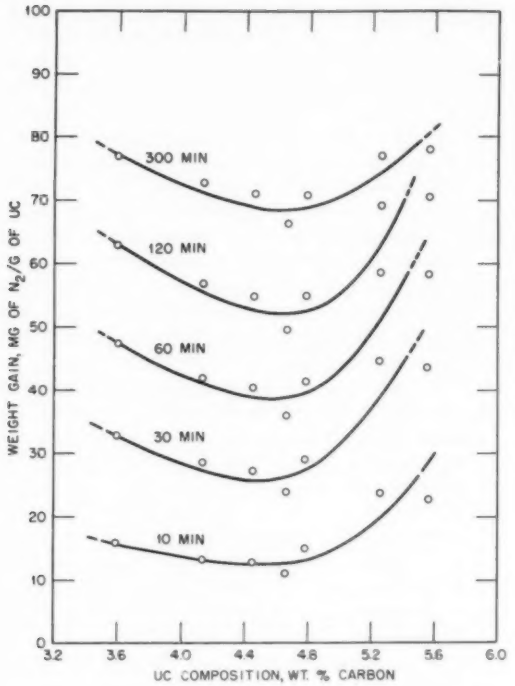

Fig. III-13 Reaction of UC with N_2 (N_2 weight gain vs. UC composition).[67]

of age occurred between about 7 and 42 days, and the effect leveled out after about 60 days. Storage of the carbide for several weeks under vacuum did not produce the aging effect.

The effect of initial particle size of the carbide on the nitridation rate is shown in Fig. III-12. The particle size of the carbide changed during the course of the reaction because of fragmentation. In general the effect of particle size above 30 mesh upon nitridation rate was negligible. From 30 to 200 mesh, the reaction rate decreased somewhat with decreasing particle size, and from 200 to −400 mesh, the rate increased sharply with decreasing particle size.

Figure III-13 shows the effect of carbon content of the uranium carbide on the nitridation rate. Minimum rates were observed at 4.6 to 4.7 wt.% carbon, indicating that slightly hypostoichiometric* uranium monocarbide is the most stable form. The most rapid rates were observed with carbide samples having the highest carbon contents (5.25 and 5.55 wt.% carbon).

Over the range of 10 to 600 mm Hg, the effect of nitrogen pressure on the rate of the nitridation reaction can be described by the equation

$$K \cong 0.033\ (P)^{3/4} \qquad (8)$$

where P is in atmospheres and K is a proportionality constant for the rate expression.

In the temperature range from 550 to 650°C, an Arrhenius plot (see Fig. III-14) is linear with a negative slope corresponding to an activation energy of 31.8 ± 1.3 kcal/mole for the primary reaction

$$UC + {}^{3}/_{4}N_2 = {}^{1}/_{2}U_2N_3 + C \qquad (9)$$

Above 650°C the slope increases, becoming zero at about 900°C; above 950°C the slope has a positive, constant value. Although it appears that a second inhibiting reaction occurs in the higher temperature region, the exact nature of this secondary reaction was not investigated.

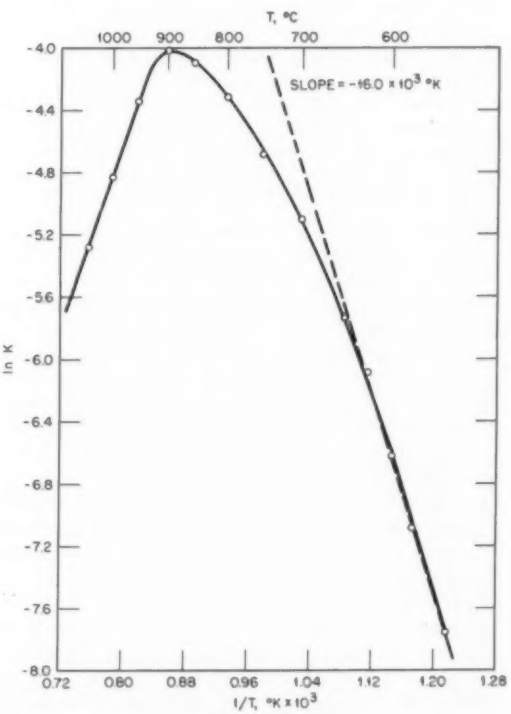

Fig. III-14 Arrhenius plot of observed nitrogen gain in UC.[67]

*The theoretical carbon content of uranium monocarbide is 4.80 wt.%.

During this study it was also found that exposure of the reaction product to air at room temperature resulted in a gradual loss of nitrogen from the product and an approximately equal rise in the oxygen content.

(R. K. Steunenberg)

References

1. J. H. Reynolds (Ed.), Nuclear Engineering Department Progress Report, September 1–December 31, 1962, USAEC Report BNL-782, Brookhaven National Laboratory, May 1963.
2. *Reactor Fuel Process.*, 6(4): 15 (Fall 1963).
3. Argonne National Laboratory, Chemical Engineering Division Summary Report for April, May, and June 1963, USAEC Report ANL-6725, December 1963.
4. C. D. Scott, L. E. McNeese, and J. C. Suddath, Processing of Graphite Fuels for Uranium Recovery by Oxidation and Fluorination, USAEC Report ORNL-TM-185, Oak Ridge National Laboratory, Mar. 20, 1962.
5. R. E. Blanco, G. I. Cathers, L. M. Ferris, T. A. Gens, and E. L. Nicholson, Processing of Graphite Reactor Fuels Containing Coated Particles and Ceramics, USAEC Report ORNL-TM-667, Oak Ridge National Laboratory, Sept. 6, 1963.
6. R. L. Jarry, L. J. Anastasia, J. Fischer, L. E. Trevorrow, T. D. Baker, and J. J. Stockbar, Laboratory Investigations in Support of Fluid Bed Fluoride Volatility Processes. Part I. The Fluorination of Uranium Dioxide–Plutonium Dioxide Solid Solutions, USAEC Report ANL-6742, Argonne National Laboratory, September 1963.
7. L. Trevorrow, J. Fischer, and J. Riha, Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part III. Separation of Gaseous Mixtures of Uranium Hexafluoride and Plutonium Hexafluoride by Thermal Decomposition, USAEC Report ANL-6762, Argonne National Laboratory, August 1963.
8. Centre d'Étude de l'Énergie Nucléaire, Mol, Belgium, Retreatment of Irradiated Fuels, Quarterly Report No. 11, October 1–December 31, 1962, USAEC Report EURAEC-634, 1963.
9. Centre d'Étude de l'Énergie Nucléaire, Mol, Belgium, Reprocessing of Irradiated Fuels, Quarterly Report No. 12, January 1–March 31, 1963, USAEC Report EURAEC-665, 1963.
10. D. Naumann, A Laboratory Study of Chlorination-Based Processing of Neutron-Irradiated Uranium Fuel Elements, *Kernenergie*, 5: 118-119 (1962); also in USAEC Translation AEC-tr-5605.
11. D. Naumann, Laboratory Study of Chlorination Processing of Neutron-Irradiated Uranium Nuclear Fuel. Part 2. Separation by Distillation of the Chlorination Products of Reactor-Irradiated Uranium Dioxide, *Kernenergie*, 6(2): 73-76 (February 1963); also in USAEC Translation AEC-tr-5908.
12. D. Naumann, Laboratory Study of Chlorination Processing of Neutron-Irradiated Uranium Nuclear Fuel. Part 3. Plutonium Separation by Gas Chromatography of the Chloride Vapor on Activated Carbon, *Kernenergie*, 6(3): 116-121 (March 1963); also in USAEC Translation AEC-tr-5951.
13. D. Naumann, Laboratory Study of Chlorination Processing of Neutron-Irradiated Uranium Nuclear Fuel. Part 4. Production and Properties of Zirconium Phosphate–Silicate Exchange Material and Its Application to Plutonium Separation, *Kernenergie*, 6(4): 173-176 (April 1963).
14. D. Naumann, Laboratory Study of Chlorination Processing of Neutron-Irradiated Uranium Nuclear Fuel. Part 5. Separation of Cesium and Regeneration of Uranium Dioxide, *Kernenergie*, 6(8): 410-411 (August 1963).
15. C. Hayman and M. C. Stuart, Fulmer Research Institute, 1963. (Unpublished)
16. J. L. Settle, H. M. Feder, and W. N. Hubbard, Fluorine Bomb Calorimetry. VI. The Enthalpy of Formation of Uranium Hexafluoride, *J. Phys. Chem.*, 67(9): 1892-1895 (September 1963).
17. *Reactor Fuel Process.*, 7(1): 40 (Winter 1963–1964).
18. J. R. Geichman, E. A. Smith, and P. R. Ogle, Hexafluorides of Molybdenum, Tungsten, and Uranium. II. Reactions with Nitryl Fluoride, Nitrosyl Fluoride and Nitrosyl Chloride, *Inorg. Chem.*, 2(5): 1012-1015 (October 1963).
19. L. E. Trevorrow, J. Fischer, and W. H. Gunther, The Reactions of Uranium Hexafluoride with Hydrogen Sulfide and with Carbon Disulfide, *Inorg. Chem.*, 2(6): 1281-1284 (December 1963).
20. L. E. McNeese, An Experimental Study of Sorption of Uranium Hexafluoride by Sodium Fluoride Pellets and a Mathematical Analysis of Diffusion with Simultaneous Reaction, USAEC Report ORNL-3494, Oak Ridge National Laboratory, Nov. 29, 1963.
21. S. Katz, Apparatus for the Gasometric Study of Solid-Gas Reactions: Sodium Fluoride with Hydrogen Fluoride and Uranium Hexafluoride, USAEC Report ORNL-3497, Oak Ridge National Laboratory, Oct. 29, 1963.
22. Oak Ridge National Laboratory, Dec. 12, 1963. (Unpublished)
23. E. N. Deichman and I. V. Tananaev, Plutonium Fluorides, *Soviet Radiochemistry (English Transl.)*, 4(1): 56-62 (January–February 1962).
24. M. J. Steindler, Laboratory Investigations in Support of Fluid Bed Fluoride Volatility Processes. Part II. The Properties of Plutonium Hexafluoride, USAEC Report ANL-6753, Argonne National Laboratory, August 1963.
25. D. H. Kelly, B. Post, and R. W. Mason, Reaction Between Fluorine and Alkali Metal Halides at Ele-

vated Pressure and Temperature, *J. Am. Chem. Soc.*, 85(3): 307-308 (Feb. 5, 1963).

26. Y. A. Luk'yanychev, N. S. Nikolaev, I. I. Astakhov, and V. I. Luk'yanycheva, A Study of the Mechanism of Copper Fluorination at High Temperatures, *Proc. Acad. Sci. USSR, Phys. Chem. Sect. (English Transl.)*, 147(1-6): 874-876 (November–December 1962).
27. A. J. Edwards, D. Hugill, and R. D. Peacock, New Fluorine Compounds of Technetium, *Nature*, 200 (4907): 672 (Nov. 16, 1963).
28. J. C. Hesson, M. J. Feldman, and L. Burris, Description and Proposed Operation of the Fuel Cycle Facility for the Second Experimental Breeder Reactor (EBR-II), USAEC Report ANL-6605, Argonne National Laboratory, April 1963.
29. R. M. Adams and A. Glassner (Comps.), Reactor Development Program Progress Report for October 1963, USAEC Report ANL-6801, pp. 18-25, 56-58, Argonne National Laboratory, Nov. 15, 1963.
30. R. M. Adams and A. Glassner (Comps.), Reactor Development Program Progress Report for November 1963, USAEC Report ANL-6808, pp. 21-26, 51-53, Argonne National Laboratory, Dec. 15, 1963.
31. R. M. Adams and A. Glassner (Comps.), Reactor Development Program Progress Report for December 1963, USAEC Report ANL-6810, pp. 9-10, 14-16, Argonne National Laboratory, Jan. 15, 1964.
32. J. Pascal and P. Lacombe, Purification of Uranium by Floating Zone Refining by Electron Bombardment, *J. Nucl. Mater.*, 9: 155-169 (July 1963).
33. N. A. de Libanati, D. Calais, and P. Lacombe, Secondary Recrystallization and Recrystallization After Cold Working by High Purity Uranium, *J. Nucl. Mater.*, 10: 23-42 (September 1963).
34. D. F. Kaufman, E. D. Levine, J. J. Pickett, and L. R. Aronin, The Effect of Zone Refining on the Purity and Mechanical Properties of Beryllium Single Crystals, USAEC Report NMI-TJ-54, Nuclear Metals, Inc., Aug. 7, 1963.
35. B. Schaub and G. Cabane, Purification of Beryllium by Zone Fission, *Compt. Rend.*, 257: 444-447 (Aug. 7, 1963).
36. M. Kobayashi, S. Maeda, T. Sawai, and H. Kurosu, Study of Purification of Aluminum by the Method of Zone Melting and Neutron Activation, Tokyo Metropolitan Isotope Centre Ann. Report (in French), 1: 33-44 (1962).
37. *Reactor Fuel Process.*, 6(3): 28 (July 1963).
38. P. Chiotti, Counter Current Extraction in Salt/Metal Systems Involving Oxidation-Reduction Reactions, USAEC Report IS-660, Ames Laboratory, June 1963.
39. L. M. Pidgeon, The Production of Reactive Metals—Retrospect and Prospect, *Trans. Met. Soc. AIME*, 227: 821-834 (August 1963).
40. G. Chauvin, H. Coriou, and J. Hure, Electrorefining of Nuclear Materials in a Molten Salt Bath (in French), *Metaux (Corrosion-Ind.)*, 37: 112-126 (March 1962).
41. W. Rafalski, Electrolytic Obtaining of Uranium and Thorium from Molten Salts, Second Yugoslavian Polish Symposium on Uranium Technology and Metallurgy, Paper CONF-207-9 (in Polish), Held in Yakopane, Poland, September 1963.
42. M. H. Curtis, Continuous Electrowinning of Plutonium from Chloride Melts, USAEC Report HW-SA-3046, Hanford Atomic Products Operation, Sept. 12, 1963.
43. J. B. Knighton, Production of Actinide Metal, U. S. Patent 3,109,731, Nov. 5, 1963.
44. R. J. Teitel, Reduction of Uranium Oxide, U. S. Patent 3,099,525, July 30, 1963.
45. J. H. Reynolds (Ed.), Nuclear Engineering Department Progress Report, January 1–April 30, 1963, USAEC Report BNL-799, pp. 74-85, Brookhaven National Laboratory, October 1963.
46. P. Chiotti, J. T. Mason, and K. J. Gill, Phase Diagram and Thermodynamic Properties of the Yttrium-Zinc System, *Trans. Met. Soc. AIME*, 227: 910 (August 1963).
47. *Reactor Fuel Process.*, 6(1): 30-31 (January 1963).
48. L. J. Wittenberg and G. R. Grove, Reactor Fuels and Materials Development Plutonium Research, July–September 1963, USAEC Report MLM-1171, Mound Laboratory, Sept. 30, 1963.
49. D. B. Novotny and J. F. Smith, Thermodynamics of Formation of $ThMg_2$, USAEC Report IS-589, Ames Laboratory, Jan. 11, 1963.
50. D. R. Stephens, The Phase Diagram of Plutonium, USAEC Report UCRL-7172, University of California Lawrence Radiation Laboratory, Feb. 8, 1963.
51. B. Spriet, Surface Tension of Uranium and Plutonium at the Melting Point, *Mem. Sci. Rev. Met.* (in French), 60: 531-540 (July–August 1963).
52. Los Alamos Scientific Laboratory, Quarterly Status Report on LAMPRE Program for Period Ending November 20, 1963, USAEC Report LAMS-3021, December 1963.
53. Brookhaven National Laboratory, High-Temperature Liquid-Metal Technology Review, Vol. 1, No. 4, USAEC Report BNL-825, August 1963.
54. J. R. DiStefano and E. E. Hoffman, Corrosion Mechanisms in Refractory Metal–Alkali Metal Systems, USAEC Report ORNL-3424, Oak Ridge National Laboratory, Sept. 16, 1963.
55. W. H. Reas, Chemical Laboratory Monthly Report, September 1963, USAEC Report HW-79046C, Hanford Atomic Products Operation, Oct. 15, 1963. (Classified)
56. W. H. Reas, Chemical Laboratory Monthly Report, October 1963, USAEC Report HW-79377C, Hanford Atomic Products Operation, Nov. 15, 1963. (Classified)
57. W. H. Reas, Chemical Laboratory Monthly Re-

port, November 1963, USAEC Report HW-79726C, Hanford Atomic Products Operation, Dec. 15, 1963. (Classified)

58. M. M. Hendrickson and J. K. Green (Eds.), Research and Development Programs Executed for the Division of Reactor Development, Quarterly Progress Report, January–March 1963, USAEC Report HW-78118, Hanford Atomic Products Operation, April 1963.
59. R. W. Stromatt, Studies on the Electroreduction of Uranyl(VI) in Molten Equimolar KCl-NaCl by Chronopotentiometric and Electrode Impedance Measurements, *J. Electrochem. Soc.*, 110: 1277-1283 (1963).
60. *Reactor Fuel Process.*, 6(2): 34 (April 1963).
61. D. E. McKenzie, Atomics International, August 1963. (Unpublished)
62. D. E. McKenzie, Atomics International, September 1963. (Unpublished)
63. D. E. McKenzie, Atomics International, October 1963. (Unpublished)
64. K. T. Scott and K. T. Harrison, Some Studies of the Oxidation of Uranium Dioxide, *J. Nucl. Mater.*, 8(3): 307-319 (1963).
65. C. Arâoz, Kinetics of the Oxidation of UO_2 in Air, Report No. 74, Argentine Report NP-12672, 1962.
66. E. E. Jackson and M. H. Rand, The Oxidation Behaviour of Plutonium Dioxide and Solid Solutions Containing Plutonium Dioxide, British Report AERE-R-3636, June 1963.
67. L. A. Hanson, Reprocessing of Uranium Carbide by a Nitride–Carbide Cycle. I. Kinetics of Nitride Formation, USAEC Report NAA-SR-8388, Atomics International, Oct. 31, 1963.

Section

IV

Reactor Fuel Processing

Waste Disposal

Liquid-Waste Treatment by Ion Exchange and Foam Separation

Ion Exchange

Skarpelos[1] at Hanford has presented a conceptual process flow sheet (see Fig. IV-1) for the decontamination by ion-exchange techniques of low-level-activity process condensate wastes. This flow sheet is based on information obtained from ion-exchange runs that were carried out in the Hanford Micro Pilot Plant (MPP).[2] These runs utilized full-plant-level-activity condensate from the self-boiling of neutralized high-level-activity wastes in the Purex tank-farm waste facility. In the flow sheet the condensate waste, which contains ammonium ion and organic material, is fed to a steam-stripper tower. The overhead vapors, representing about 5% of the condensate waste, contain most of the ammonium ion and organic material; some iodine and ruthenium are also present. The ammonium-bearing aqueous phase is separated from the organic phase by means of a decanter. The organic phase, which represents about 0.02% of the condensate waste, contains most of the ruthenium and iodine in the overhead stream, and further processing may be necessary. The aqueous phase, which contains almost none of the radioisotopes, can be disposed to the environment without further treatment.

The bulk of the waste leaves the stripping tower as bottoms. This stream is cooled and then passed through a precoat type filter which uses a cesium-selective adsorbent (100 to 400 mesh) such as clinoptilolite or Decalso as a filter aid. This filtering step removes particulate matter and cesium. The adsorbent cake is discharged for burial whenever its cesium capacity is exhausted or whenever the pressure drop across the filter reaches a predetermined value. The filtered waste is then passed through a strong-base anion bed that removes an appreciable amount of the ruthenium, along with nitrate and nitrite ions. Periodically, this bed is regenerated with sodium hydroxide. The regenerant solution is discharged to an underground tank storage. Since alkali in excess of the stoichiometric amount must be used, the regenerant solution could be used for neutralizing high-level-activity acid wastes. The effluent stream from the anion bed is acidified to *p*H 4 before it enters the cation bed which removes strontium, cerium, zirconium, residual cesium, and other cationic isotopes. The cation resin has an extremely high capacity for these radioisotopes and can economically be discharged for burial. The effluent from the cation bed is sufficiently decontaminated so that it can be safely discharged to the environment. If the residual acid in the effluent from the cation resin column needs to be neutralized, the effluent can be combined with the aqueous overhead stream containing ammonium ion.

The cost for the decontamination of a radioactive condensate waste based on this ion-exchange process was estimated at $7.50/1000 gal of waste for a fuel-processing plant having a processing capacity of 2 tons/day and producing about 30,000 gal of condensate per day. This estimated cost for treatment of the condensate waste by an ion-exchange process is less than one-half of that estimated for treatment by an evaporative process. It is believed that the cost to treat an acidic condensate by an ion-exchange process would cost about the same as for a basic condensate.

The installation of equipment was completed for pilot-plant demonstration of this ion-exchange process for the treatment of Purex tank-farm condensate.[3]

At Hanford, batch equilibrium experiments were conducted to determine the effectiveness of anion-exchange resins (nitrite form) for the removal of ruthenium in the presence of nitrite ion from steam-stripped Purex tank-farm condensate. Nitrite ion is the predominant anion (5 to 10 ppm) in the steam-stripped condensate.[3] nitrite breakthrough. Therefore, in the selection of an ion-exchanger resin in the hydroxyl form for maximum ruthenium loading, both ruthenium selectivity and the total capacity of the exchanger for nitrite must be considered.

Experimental work is also under way at Hanford to evaluate electrodialysis[3] as a pro-

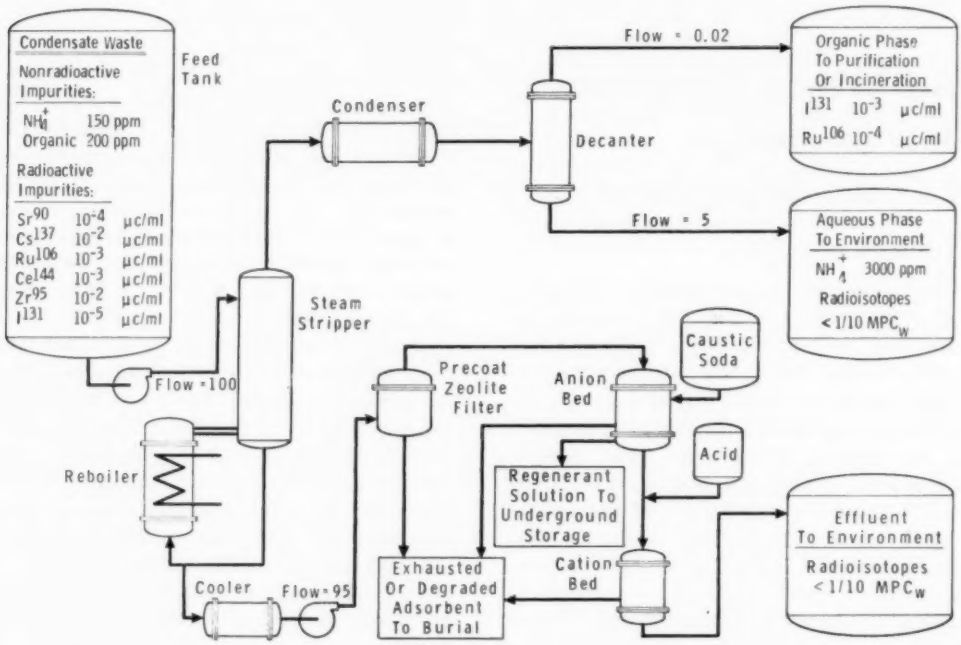

Fig. IV-1 Condensate decontamination flow diagram.[1]

The highest distribution coefficients for ruthenium, which ranged from 120 to 130, were obtained with Duolite A-14, Amberlite IR-400, and Dowex 1-X8. The test results also showed that, with the resins in the nitrite form, the adsorption of ruthenium by Dowex 1-X8 was greater than that by Dowex 1-X4, indicating that greater adsorption of ruthenium from the steam-stripped condensate was achieved with increased cross linkage of the resin.

Although the resins noted above have the highest selectivity of those tested for ruthenium in the presence of nitrite, they do not necessarily have the highest capacity for ruthenium in the steam-stripped condensate waste. In previous ion-exchange (hydroxyl form) experiments with steam-stripped condensate waste, ruthenium breakthrough occurred along with the

cessing technique for the treatment of low-level-activity and intermediate-level-activity wastes. The main applicability of electrodialysis appears to be in the pretreatment of wastes to extend the bed life of adsorbent columns; however, it may also be beneficial in ruthenium removal.

ICPP Adsorption Studies with Naturally Occurring Earth Materials

Wilding and Rhodes[4] at the Idaho Chemical Processing Plant (ICPP) have reported on the results of laboratory adsorption tests that were carried out on naturally occurring earth materials from eastern Idaho. The tests were conducted to determine the ability of these materials to remove radioisotopes from low-level-activity wastes originating at the National Reactor Test-

ing Station (NRTS), Idaho. Three earth materials that included a lignite, a claylike material, and a mineral (clinoptilolite) were selected as being representative of the many materials considered.

The results of the laboratory experiments showed that cesium, strontium, cobalt, cerium, ruthenium, and chromium were adsorbed on locally available earth materials under favorable conditions. In batch equilibrium experiments the highest distribution coefficients for cesium and strontium occurred in the range of *p*H from 6.0 to 9.0. Materials with cation-exchange capacities greater than 0.3 meq/g [clinoptilolite, 0.35 meq/g; clay-bearing material (MTR-12-3), 0.67 meq/g; lignite (sample no. 4), 1.08 meq/g], in general, had distribution coefficients for cesium and strontium of 1000 or greater in this *p*H range. Below *p*H 6.0 and about *p*H 9.0, the distribution coefficient usually decreased. However, over the *p*H range 1.0 to 10, clinoptilolite had a distribution coefficient for cesium greater than 1000.

The effect of the complexing agents, citrate and ethylenediaminetetraacetic acid (EDTA), on the adsorption of strontium, ruthenium, cerium, chromium, and cobalt by the earth materials was also determined. In nearly all systems studied, appreciable amounts of all isotopes were adsorbed by the earth materials. Citrate had a definite depressing effect on ruthenium adsorption. EDTA lowered the distribution coefficient of the five isotopes tested, in some cases by a factor of 2 or more. EDTA decreased the adsorption of strontium, cobalt, and ruthenium more than the adsorption of cerium and chromium. Iron or another material of similar characteristics should be added to "tie up" the complexing agents when appreciable amounts of the complexing agents are present.

The claylike materials dispersed relatively easily in solution, especially in the alkaline *p*H range, forming colloidal particles that were very impervious to water flow. Obviously these materials would not be suitable for use in fixed-bed exchangers. However, they might be suitable as scavenging agents in a batch process. Lignites had relatively high exchange capacities but tended to decompose in alkaline solutions. In addition, when wetted, they tend to swell and decrease flow rates. The mineral clinoptilolite, on the other hand, has good physical and good ion-exchange characteristics over a wide *p*H range and is easily prepared in any desired particle size. Although clinoptilolite is very selective for cesium, it also has a fairly good capacity for strontium, as well as for most of the other cations studied.

Columnar ion-exchange experiments were carried out in which a low-level-activity waste (water from the ICPP fuel storage basin) was passed through separate columns of Dowex 50W-X8 (an organic cation-exchange resin) and clinoptilolite. The results of these tests indicated that cesium breakthrough was limiting for the Dowex 50W-X8 resin and strontium breakthrough was limiting for the mineral column. However, because of the simplicity of equipment, low daily operating costs, and ease of handling and storage considerations, a clinoptilolite fixed-bed system will be installed at the ICPP fuel storage basin to decontaminate the basin water (some 10,000 gal/day) before it is discharged to the environment. The expended clinoptilolite units will be replaced periodically and buried with other solid waste materials.

ORNL Scavenging Ion-Exchange Process Studies

Oak Ridge National Laboratory (ORNL) is continuing the development of a scavenging ion-exchange process for the decontamination of the large volumes of slightly contaminated water which originate from many sources in the processing of nuclear fuels.[2,5] This process employs a head-end treatment step which involves precipitation of a portion of the activity with sodium hydroxide, clarification of the water in a gently agitated sludge-column clarifier, and filtration of the effluent from the clarifier unit. The clarified and filtered effluent is then passed through a carboxylic-phenolic resin for sorption of Cs^{137} and Sr^{90}.

During the head-end or precipitation portion of the process, the presence of phosphate in the waste stream hinders the precipitation and removal of calcium and magnesium ions (which, if not removed, would load the cation-exchange column). The treatment of the low-level-activity waste with a sorbent material prior to the head-end treatment step was studied as a means of reducing the concentration of phosphate in the waste stream.

In laboratory-scale tests, ORNL low-level-activity waste (LAW) was flowed upward through a column of activated alumina (F-20 grade; 80 to 200 mesh; Aluminum Company of America). The alumina reduced the phosphate concentration

of the LAW from about 3 ppm to 0.2 to 0.5 ppm during treatment of about 8700 column volumes of waste. This treatment permitted more nearly quantitative precipitation of the hardness ions in the scavenging-precipitation clarifier; the residual hardness ions of the clarified overflow stream was reduced from the 70 ppm that was usually present to less than 10 ppm.

In other laboratory tests a 1000-ppm orthophosphate solution (*p*H 7) was passed through a column of activated alumina and a column of an anion (TAD-1) resin. The anion resin sorbed phosphate from 22 bed volumes of the orthophosphate solution as compared to 10 bed volumes of the same solution for the alumina. More than 90% of the phosphate was eluted from the anion resin with about one bed volume of 1*M* NaOH.

Foam Separation

ORNL is continuing its investigation of the removal of Sr^{90} from ORNL LAW by means of foam-separation techniques.[2,5,6] Development work on two foam-separation flow sheets in laboratory-scale equipment (a one-step process and a two-step process) is carried out.[5,6] It has been shown[7] that the large amounts of calcium (60 to 70 ppm as $CaCO_3$) present in the LAW interfere with Sr^{90} removal by foam separation. In both flow sheets a large fraction of the calcium is precipitated in a scavenging-precipitation step prior to foam separation.

The one-step process involves precipitating the calcium as the orthophosphate in a small premixer-precipitator and then feeding the resultant solution and solids to a foam-separation column. Tests have been conducted with simulated ORNL LAW (Sr^{85} activity added as a tracer element) to which was added phosphate ion (67 ppm), ferrous ion (23 ppm), Siphonate DS-10 foaming agent (90 ppm), Armeen Z flotation agent (15 ppm), and sodium hydroxide (to adjust *p*H to 11.5). The solution and the precipitate that was formed after the *p*H adjustment and during the holdup (10 to 20 min) in the premixer were fed continuously into a 2-in.-diameter multistage foam-separation column. With a liquid feed throughput of 30 gal/(sq ft)(hr), and a gas-to-liquid feed ratio of 12.4 (for the best decontamination factor for strontium), a strontium decontamination factor in excess of 1000 was achieved. The decontamination factor increased as the gas-to-liquid ratio and the height of the foam column below the feed distributor were increased. In preliminary tests of the one-step process with actual ORNL LAW, strontium decontamination factors of 200 to 300 were achieved.

The two-step process carries out the removal of most of the calcium as the orthophosphate or the carbonate in a upflow sludge column from which the unfiltered effluent is fed to a foam-separation column for removal of strontium. Preliminary runs were conducted with ORNL tap water which contained added Sr^{85} tracer. Sodium hydroxide (0.005*M*) and sodium carbonate (0.005*M*) were added to precipitate the calcium and magnesium hardness ions (final *p*H of resulting solution, 11.3); iron (Fe^{3+}, 5 ppm) was added as coagulant. The foaming agent sodium dodecylbenzene sulfonate (NaDBS) was added both to the effluent from the sludge column (50 ppm) which was fed to the foam column and to the bottom of the foam column (12 ppm). Depending on the run conditions for the foam column, strontium decontamination factors for the foam column ranged from 2 to greater than 400 and for the overall process ranged from 320 to greater than 15,000.

Conversion of High-Level-Activity Wastes to Solids

Spray Calcination

Hanford is continuing to study radiant-heat spray calcination[8] as a method for the treatment of Purex-process high-level-activity aqueous wastes. In radiant-heat spray calcination, the feed solution is sprayed into the top of a heated column that is maintained at 700 to 750°C. Spray droplets are converted to solids, and some salt decomposition is achieved. The dried residue falls into a melt pot that is used to effect a reduction in volume of the residue. In the melt pot, which is maintained well above the melting temperature (typically 750°C) of the dried residue, further decomposition and melting of the dried residue take place continuously.

In a recent spray-calcination run,[3] sugar was added to ammonia-neutralized full-plant-level-activity Purex waste (1WW) to determine its

effect on the suppression of ruthenium volatility. With the addition of 30 g of sugar per liter of neutralized 1WW, the ruthenium found in the condensate amounted to 1% of the original ruthenium present in the 1WW, which was greater than for a previous run[9] in which the acidic 1WW waste was made alkaline (*p*H 10) with sodium hydroxide and to which sugar was added.

In two other spray-calcination runs, phosphoric acid and sodium nitrate were added to the full-plant-level-activity Purex waste (1WW). In one of these runs, 100 g of sugar per liter of 1WW was also added. Calcines produced from wastes which contain added phosphate are less soluble in water than calcines from wastes which do not contain added phosphate; the lower solubility is advantageous for safe long-term storage. The sodium nitrate was added to form a low-melting calcine. In both runs, melts were obtained in a pot held at 900°C. The behavior of the fission products was not strongly affected by the addition of phosphoric acid. The decontamination factors (greater than 1×10^8) for the fission products in the off-gas (after final treatment with absolute filters) were similar to those obtained with acidic Purex 1WW wastes which did not contain additives. The addition of sugar suppressed the volatilization of ruthenium to the condensate; the ruthenium found in the condensate was 0.8% of the amount originally present in the feed. This result may be compared with the result of a previous run made with acidic Purex 1WW waste (with sugar added) in which the ruthenium found in the condensate was 3% of the amount initially present in the feed.

The behavior of iodine (which would be present in short-term cooled wastes) was investigated in a run that was carried out in an 8-in.-diameter nonradioactive pilot spray calciner. A simulated Purex 1WW, which had been treated with sugar (to destroy excess HNO_3 as in current plant waste-management practice) and which contained added I^{131} tracer (as NaI), was used as feed material. The full-plant-level-activity Purex 1WW wastes used in previous spray-calcination runs have been long-term cooled, and the iodine has not been considered a problem. The preliminary results indicate that 80% of the iodine is volatilized from the calcine and that only a portion of it is found in the condensate. A low sodium carry-over to the condensate was noted which would infer that the iodine was in a volatile form rather than a particulate form when going to the condensate.

Pot Calcination

At ORNL a pot-calcination process is being studied for converting high-level-activity wastes to solids.[10] As part of this investigation, corrosion studies[5] have been carried out to determine the rate of corrosion of welded specimens of Hastelloy F, type 304L stainless steel, titanium 45A, and couples of 304L stainless steel with titanium 45A. The specimens were exposed to the vapor and solution phases of boiling simulated Hanford formaldehyde-treated Purex acidic wastes (FTW-65). These wastes will be produced at Hanford in 1965. The results of tests which were conducted for 1300 to 1600 hr showed low rates of corrosion for specimens of type 304L stainless steel and titanium 45A in both the coupled and uncoupled form; the maximum rate was for the coupled type 304L stainless-steel specimen and amounted to 0.3 mil/month with no local attack.

Final Disposal Methods

Engineering, Economics, and Safety Evaluation

As part of its continuing study of the economics of high-level-activity waste management,[11] ORNL has prepared a report[12] that examines the relative costs of concrete vaults and granite and salt formations for the final disposal of cylinders of calcined radioactive wastes.

In the United States, cavities mined in natural salt formations are believed to offer the best possibilities for permanent disposal of these wastes. In addition to its abundance and wide distribution, salt offers the advantages of impermeability, good thermal conductivity, and high compressive strength. The use of salt, however, implies the probable need for shipping the waste to a salt mine from a fuel-processing plant that may possibly be many miles distant. Suitable deposits of granite or shale might be more accessible to a plant, and it is conceivable that high-integrity concrete vaults could be constructed at the plant site to serve the purposes of permanent containment.

As in previous cost studies in this series,[11] the analysis is made on the basis of a 6 metric

ton/day power-reactor fuel-processing plant, which is designed to process 1500 metric tons of uranium converter fuel per year at a burnup of 10,000 Mwd/metric ton and 270 metric tons of thorium converter fuel per year at a burnup of 20,000 Mwd/metric ton. Acid Purex and reacidified Thorex waste were chosen for this study, since they possess the highest and lowest heat-generation rates per unit volume, respectively.

After the waste has been placed in storage, all accesses to the storage area are sealed to provide the maximum containment and isolation from the environment. Under these circumstances, dissipation of the radioactive decay heat will occur only by conduction through the surrounding solid medium. Better heat transfer permitting more efficient utilization of storage space could be achieved by circulating air through the storage area and discharging it back into the atmosphere after appropriate monitoring and/or cleaning. However, this would represent a less safe situation, in that it would provide a direct route for escape of the fission products into the environment in the event of a natural disaster.

The storage of calcined solid wastes in concrete vaults involves the construction of concrete rooms which are completely buried and which have just sufficient earth cover to provide the necessary shielding. In concept, the vaults would be similar in their gross features to many of the tanks built for storage of liquid radioactive wastes, in that they would be underground structures of reinforced concrete with about 10 ft of earth cover and a floor-to-ceiling height of about 15 ft. For purposes of assessment the vaults were considered to be sealed completely from the surface in order to make storage in them as safe as possible; and space requirements were calculated assuming dissipation of the heat of radioactive decay by conduction through the earth cover. Vaults of two types of concrete were evaluated: ordinary concrete, capable of withstanding a temperature of 400 to 500°F, and "high-temperature concrete," capable of withstanding a temperature of 1000°F.

The spacing between cylinders in a storage system is controlled by the necessity to dissipate the heat generated by radioactive decay without reaching temperatures injurious to the storage system. A minimum storage age occurs when the calcined waste and the concrete are simultaneously at their maximum allowable temperatures. For greater ages the temperature of the concrete controls the spacing between cylinders. Calculations of space requirements for acid Purex and reacidified Thorex wastes situated in racks in high-temperature concrete vaults and in salt rooms show that the greatest savings in space requirements for vaults over the use of salt formations occur for storage after the waste has aged from 10 to 30 years, and that over this range of ages the space requirements differ by a constant factor. The results for a storage age of 30 years (Figs. IV-2 and IV-3)

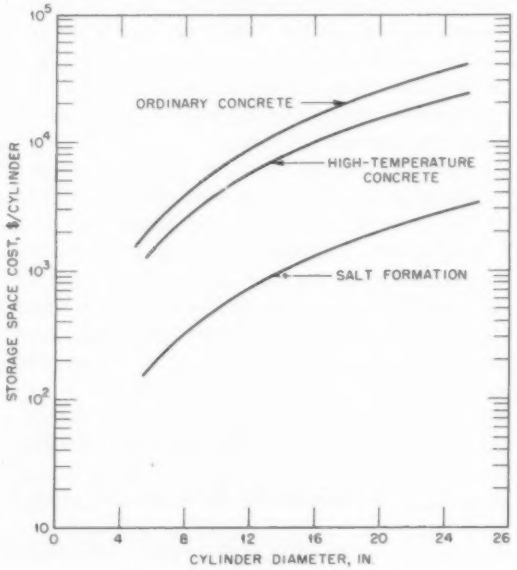

Fig. IV-2 Cost of storage space for acid Purex waste in concrete vaults and salt formations for waste aged 30 years (Ref. 12).

show that high-temperature concrete results in lower costs than ordinary concrete. However, the cost of storage space in concrete vaults is higher by a factor of 8 for both acid Purex waste and reacidified Thorex waste than the cost of storage space in salt formations.

Space requirements for storage of calcined wastes in rooms mined out of granite formations are about the same as for storage in salt formations. However, mining costs are higher for granite because heavier equipment is required, drilling is more difficult and slower, and costs for explosives are higher. If other costs (e.g., handling equipment and labor for

storing the cylinders of calcined waste) are assumed to be the same, storage in granite formations would cost about twice as much as storage in salt formations.

The authors have stated that, although costs given in the report should be valid for comparative purposes, other considerations may affect them when they are used to optimize the total costs of waste management. Although disposal in concrete vaults has been estimated to be several times more expensive than disposal in salt formations, consideration might be given to the fact that a concrete vault located at the plant site would eliminate the need for waste shipment. Although the costs for shipment of long-term decayed wastes in the largest diameter cylinders would be 10% or less of disposal costs, shipment of the wastes in smaller cylinders after short periods of decay could amount to as much as 25 to 50% of the costs of disposal in vaults. Although the potential existence of a less safe storage situation should be recognized, the vaults could be equipped, with moderate increase in cost, with forced-air convection cooling to serve as interim storage facilities until the fission-product heat generation had dropped to levels that would allow the vault to be finally sealed. In this way, interim storage in canals[11] prior to permanent disposal could be avoided. Of course, these same considerations would apply to granite or salt should the fuel-processing plant be situated adjacent to suitable deposits of either. The authors believe, however, that salt storage offers the greatest safety and that the costs, even allowing for moderate shipping costs, are less than for other alternatives.

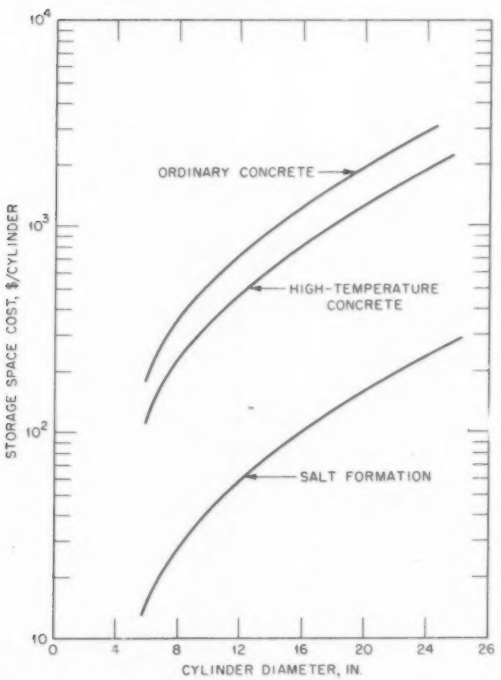

Fig. IV-3 Cost of storage space for reacidified Thorex waste in concrete vaults and salt formations for waste aged 30 years (Ref. 12).

Calcined Solids Storage in Salt Mines

A demonstration of the disposal of high-level radioactive waste solids is being designed for the Carey Salt Company mine in Lyons, Kans.[13] The objectives of the test are (1) demonstration of handling equipment and techniques; (2) determination of possible gross effects of radiation on hole closure, floor uplift, and salt-shattering temperature in an area where salt temperatures are in the range 100 to 200°C; (3) determination of possible radiolytic production of chlorine; and (4) collection of information on creep and plastic flow of salt at elevated temperatures which can be used later to design an actual disposal facility.

Fourteen irradiated Engineering Test Reactor (ETR) fuel assemblies, contained in seven cans, will supply radiation in lieu of actual solidified wastes.[5,14] The assemblies will be placed in a circular array of holes in the floor, with one can in the center and the other six cans located peripherally, spaced 5 ft on centers. The test will last two years. An identical array with electric heaters only will be operated as a control to determine the effect of radiation and heat on the salt characteristics. A proposed layout for the hot demonstration room is shown in Fig. IV-4.

The disposal hole for the demonstration with fuel elements differs from the plans for actual waste disposal in salt in that a metal liner is used in the hole to prevent contact of the fuel capsule with the salt. This liner should minimize corrosion problems and prevent hole closure by salt flow so that the fuel capsule may be recovered. A concept of the hole liner and associated components are shown in Fig. IV-5. In order to measure salt movement and sample the gases that are released from the salt as a

result of the radiation and heat emitted from the fuel capsule, an annulus approximately 2 in. wide is allowed in the region surrounding the hole liner adjacent to the fuel elements. Supplemental shielding in the form of steel shot is provided in the annular space above the fuel elements to protect personnel at the surface from radiation. Additional shielding above the fuel capsule will probably be necessary. The liner with the top cover and seal in place provides a secondary containment vessel to avoid release of radioactive material into the salt mine. Tubes for sampling gas are brought out to a junction box that connects them to gas samplers. Heaters in the annulus will supplement the heat emitted from the fuel elements and provide closer approximation to the heat generated by solid radioactive waste. The liner and junction boxes will be set in concrete to hold the assembly in place.

Since the ultimate disposal of high-level radioactive solids in salt is expected to be carried out in holes in the floor of mined openings, knowledge of behavior of rectangular rooms under the influence of elevated temperatures is important.[5]

Theoretical solutions exist for stress distributions around cylindrical openings in an elastic medium and for plastic closure of cylindrical openings at elevated temperatures for certain limited conditions. However, for rectangular openings, the only theoretical solutions known to exist are for the stress distributions in an elastic medium around openings with rounded

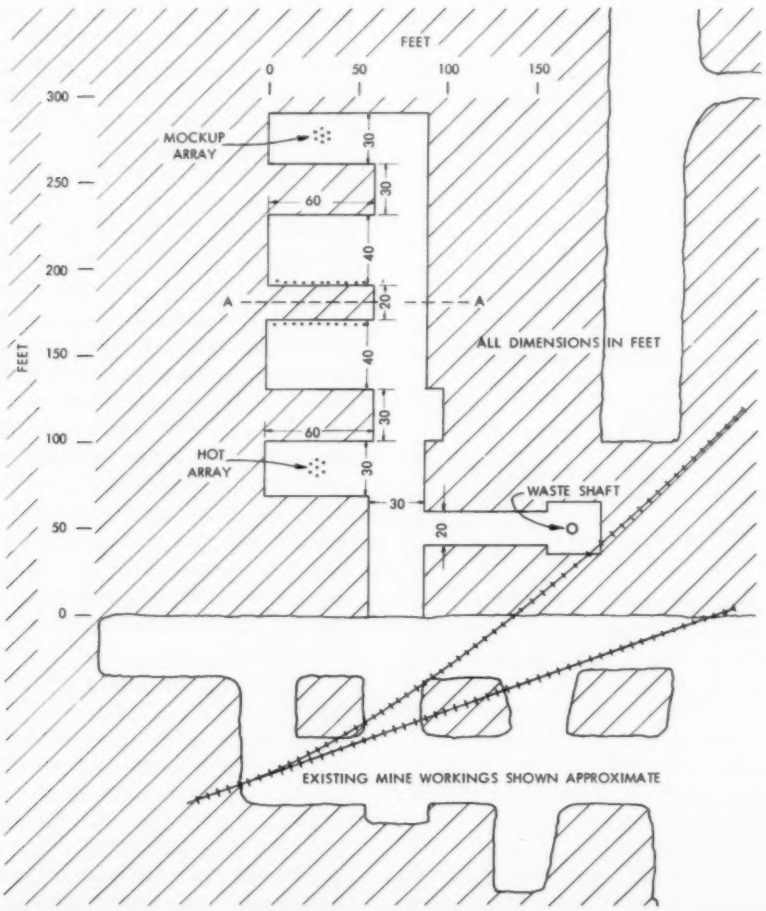

Fig. IV-4 Proposed layout for hot demonstration area.[5]

corners. Even in the case of cylindrical openings, it has not yet been established how well the theoretical solutions will predict the thermal flows that will take place in an actual salt formation.

Thus it is necessary to heat both cylindrical and rectangular openings to obtain valid data. Since the electrical energy requirements for heating an actual mine room are extremely high, studies of this nature are best carried out with scale-model openings. To study the effect of temperature on a rectangular room of proportions similar to a mine room, an opening, 8 ft wide by $9\frac{1}{2}$ ft deep by 2 ft high, has been created in the face of a large pillar in the Hutchinson, Kans., mine of the Carey Salt Company.

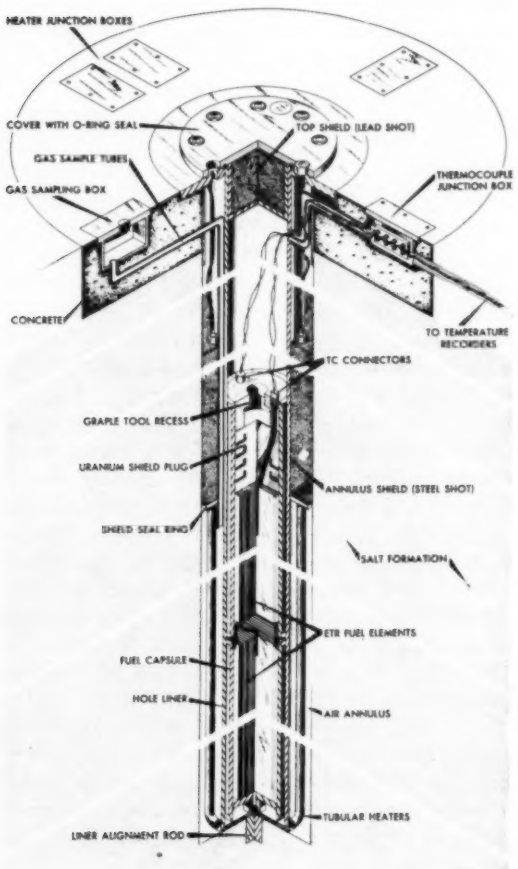

Fig. IV-5 Concept of fuel capsule, hole liner, and shielding—radioactive solids disposal demonstration.[5]

Chloride Release from Gamma-Irradiated Salt

The storage of high-level wastes in salt formations will expose the surrounding salt to radiation, and the dose in the immediate proximity of the packaged wastes is expected to be as high as 10^{10} rads.[14] Although it is known that radiation will cause some damage to alkali halides, there has been no definitive work to prove or disprove the release of free halogen from sodium chloride. The only work found in the literature which seems to be related to this problem is that of Epstein,[15] who gives quantitative data on the amount of oxidizing substance (presumably chlorine) formed in solid potassium chloride upon exposure to high levels of gamma or beta radiation. Epstein placed an upper limit of 0.5% of the total oxidizing power generated within the solids which escapes to the gas phase. (The oxidizing power stored within the crystalline solid was determined by dissolving the solid in water and determining the oxidizing equivalent against potassium iodide or *o*-tolidine.) Values of G (number of molecules produced per 100 ev of energy absorbed) were found to decrease with dose—from 1.47×10^{-2} at 2×10^{7} rads to 5.1×10^{-4} at 3.27×10^{9} rads.

At ORNL, sodium chloride has been gamma irradiated at the steady-state temperature (35 to 60°C) of a 10,000-curie Co^{60} source, as well as at temperatures up to 250°C (Ref. 14). No release of chlorine to the vapor phase has been detected by gas chromatography or by chemical methods in the irradiations performed at 35 to 60°C with doses up to 8×10^{9} rads and at 250°C with 3×10^{8} rads. The G values for the production of oxidizing power generated in the solid decreased with dose. These values for sodium chloride at 35 to 60°C are nearly an order of magnitude less than those given by Epstein for potassium chloride at equivalent doses.

White, crystalline sodium chloride changes color with increased doses of irradiation. At 10^{6} rads it is light tan; it progressively deepens to brown and finally to a dark blue-black at about 5×10^{8} rads. Color produced by irradiation can be removed by annealing. The annealing process is temperature dependent; it is essentially complete in a few hours at 250°C, but it requires nearly a week at 190°C. When salt is irradiated at elevated temperatures, the resultant color depends on which process is faster—the accumulation or the annealing of the color centers. For example, at 160°C, accumulation

predominates, and the salt becomes colored; but at 250°C the annealing process predominates, and the salt remains white. As a result the salt irradiated at 250°C still retains oxidizing power even though it shows no apparent change in color.

The *G* values obtained by the irradiation at the lower temperatures were used to calculate the oxidizing power that would be produced in the surrounding salt during a storage period. These values are given in Table IV-1. The *G* values used for the higher dose rates were obtained by extrapolating the values obtained at 35 to 60°C. The temperature of the zones receiving doses of 10^9 rads or greater is expected to hover above 200°C, and the *G* values for these zones are expected to be lower than those used in the table.

Table IV-1 YIELD OF OXIDIZING AGENT WITH DOSE[14]

Dose, rads	*G*	Moles of oxidizing substance per gram of salt	Mass of salt irradiated, g	Total moles of oxidizing agent produced
10^6	9×10^{-3}	9×10^{-9}	1.4×10^7	0.2
10^7	3.7×10^{-3}	3.7×10^{-8}	6.8×10^6	0.4
10^8	1.4×10^{-3}	1.4×10^{-7}	3.6×10^6	0.3
10^9	7×10^{-4}	7×10^{-7}	1.5×10^6	1.0
1.2×10^{10}	2×10^{-4}	4×10^{-6}	2.9×10^5	0.7

The probable rate of production of chlorine for a calcined Purex type waste that had been cooled two years before burial is shown in Table IV-2.

Table IV-2 PROBABLE RATE OF FORMATION OF CHLORINE IN SOLID NaCl[14]

Time after burial	Dose, rads	Total chlorine produced, %
20 days	8.6×10^6	8.5
40 days	1.7×10^7	11.0
80 days	3.4×10^7	14.0
160 days	6.9×10^7	17.0
320 days	1.4×10^8	21.0
1.75 years	3.8×10^8	30.0
3.5 years	7.5×10^8	38.0
7 years	1.5×10^9	49.0
14 years	3×10^9	63.0
28 years	6×10^9	80.0

Disposal by Hydraulic Fracturing into Shale

ORNL is continuing its investigation to determine the feasibility of disposing liquid radioactive waste by mixing it with cement, or some other hardening agent, and then injecting the slurry deep into bedded rock through a specially constructed well.[5,14,16] The pressure developed at the bottom of the well forces the rock to fracture. Under favorable circumstances the fracture occurs along the bedding planes and thereby allows the waste cement mixture to flow out into the rock in a thin horizontal sheet where the waste hardens. This method may make possible the disposal of the large volumes of intermediate-level-activity wastes that are produced at ORNL.

A waste-mix slurry was tested at ORNL which was prepared with ORNL plant intermediate-level-activity waste.[5,14] The stable chemical and the radiochemical analysis of this ORNL waste are shown in Table IV-3. The slurry was prepared by mixing 265 cm^3 of ORNL waste, 454 g of Portland cement, about 27 g of bentonite, about 2.3 g of CMHEC (carboxymethylhydroxyethyl cellulose), and about 4 g of calcium lignosulfonate. The fluid loss for the slurry and the radiochemical content of the filtrate from the fluid-loss test were determined. The term "fluid loss" is a measure of the amount of liquid that would be lost from a slurry to a permeable formation; it is measured by a standard test in which the quantity of fluid lost in 30 min across 3.5 sq in. of 325-mesh screen is determined at various pressures.

The fluid loss was 30 cm^3/30 min at 100 psi for the plant waste as compared with 48 cm^3/30 min at 100 psi for a simulated ORNL intermediate-level-activity waste.* The concentrations of Sr^{90}, Cs^{137}, and Ce^{144} in the fluid that

*The composition of the simulated ORNL intermediate-level-activity waste solution was: 0.317*M* $NaNO_3$, 0.219*M* NaOH, 0.037*M* Na_2SO_4, 0.025*M* NH_4NO_3, 0.022*M* $Al(NO_3)_3$, 0.006*M* NaCl.

Table IV-3 COMPOSITION OF ORNL WASTE[14]

Stable-chemical analysis of waste		Radiochemical analysis	
Ion	Concentration, M	Radionuclide	Waste concentration, dis/(min)(ml)
Na^+	0.1	Sr^{90}	6.34×10^3
OH^-	0.04	Cs^{137}	1.44×10^6
NO_3^-	0.029	Ru^{106}	1.84×10^6
CO_3^{2-}	<0.0005	Ce^{144}	6.54×10^3
SO_4^{2-}	0.0005	Co^{60}	1.3×10^3
SO_3^{2-}	0.00025	$Zr-Nb^{95}$	780
Cl^-	<0.001	Gross beta	3.0×10^5*
Al^{3+}	0.001	Gross gamma	4.4×10^5*
K^+	0.0004		
Mg^{2+}	0.0004		

*Counts/(min)(ml).

separated from the grout were less than 10% of those in the plant waste. Ruthenium-106 and Zr^{95}-Nb^{95} were not as well retained by the waste-mix slurry; about 80% of the Co^{60} was found in the separated fluid.

A waste-mix slurry specimen that had been cured for five days at 80°F was immersed in demineralized water for leach testing. After 17 days of leaching, Co^{60} and Cs^{137} were found in the leach solution. The cesium amounted to about 7% of the original Cs^{137} present in the plant waste. The test was repeated with a specimen cured for 28 days; the Cs^{137} loss was lower by a factor of 2 (Ref. 14).

Ruthenium was the major nuclide detected in the filtrate from the fluid-loss test, but it was not detected in the water used to leach the five-day-cured specimen. Cobalt appears to be difficult to contain in this waste-mix slurry system and was found in both the fluid-loss filtrate and the leaching solution.[5] The amount of cesium detected in the leach water, assuming the activity to be due entirely to this element, is slightly higher than the observed activity noted when a simulated ORNL plant waste that contained added cesium was used. A possible reason for the higher leachability of actual plant waste may be the presence of potassium (see Table IV-3) in the waste solution, which competed with trace cesium for exchange sites on the bentonite.

Recovery of Fission Products

Horner, Brown, Crouse, and Weaver[17–19] at ORNL have presented an integrated solvent-extraction flow sheet (see Fig. IV-6) for the recovery of fission products (strontium, rare earths (mixed or separated), cesium, and zirconium-niobium) from a Purex plant waste (1WW) currently produced at Hanford. (Purex 1WW waste is the evaporation-concentrated aqueous raffinate from the tributyl phosphate–nitric acid extraction process used to recover plutonium and uranium from spent uranium reactor fuel.) The flow sheet is based on processes that have been demonstrated on a laboratory scale, namely:[18] (1) strontium and mixed rare-earth recovery by extraction with di-2-ethylhexyl phosphoric acid (D2EHPA) and its sodium salt (NaD2EHPA), (2) individual rare-earth separations with tributyl phosphate, (3) zirconium-niobium recovery by extraction with D2EHPA, and (4) cesium recovery by extraction with selected substituted phenols. Feed pretreatment methods shown in the flow sheet utilize amine extraction for the removal of bulk impurities, which include the following: nitric acid, sulfate and iron, and certain fission products (zirconium-niobium and ruthenium).

Cs^{137}, Sr^{90}, and Pm^{147} Recovery at Hanford

At Hanford, investigations have continued on the development of ion-exchange processes for the removal and purification of cesium from various high-level-activity Purex and Redox plant wastes.[2,3] Ion-exchange experiments[3] were carried out which tested the removal of cesium by various ion-exchange materials from simulated solutions of three plant wastes. The first plant waste studied was an "aqueous sludge leach" solution which originates from the water wash of the sludge remaining in the Purex plant waste tanks following the removal of the supernatant solution. The aqueous sludge leach solution is expected to contain most of the cesium and to be about $2M$ to $3M$ in sodium ion. Of the ion-exchange materials tested, a zeolite exchanger (Linde AW-400) proved to be the best. At a flow rate of 4 column volumes per hour, the breakthrough for cesium was 1% and 50% at 120 and 300 column volumes, respectively.

The second plant waste examined was an acidic Purex plant waste (FTW-65) which was made basic (pH adjusted to 10) and then filtered or centrifuged; the sodium ion content was about $1.5M$. The FTW-65 Purex waste is a high-level-activity acid waste that is expected to be produced at Hanford in 1965 and has been treated

with formaldehyde for partial acid destruction. The tests were carried out with Linde AW-400 zeolite. The results of the tests showed that, with a feed flow rate of 4 column volumes per hour, the breakthrough for cesium was 1% and 50% at 130 and 170 column volumes, respectively.

The third plant waste investigated was a high-level-activity acid Redox waste which is about 2*M* for both sodium ion and aluminum ion. In tests with clinoptilolite as the ion-exchange material, cesium loading was not satisfactory, with cesium breakthrough occurring at less than 10 column volumes.

The removal of cesium from Redox plant alkaline supernatant wastes[1,2] by means of Duolite C-3 cation-exchange resin continued to be studied. The feasibility of using fine mesh Duolite C-3 resin to improve the kinetics of cesium removal was investigated. Pressure-drop data[3] were first obtained for various mesh sizes of Duolite C-3 resin. Water and simulated alkaline supernatant solution (SX) were passed at various flow rates through columns containing 20 to 40, 40 to 60, and 20 to 60 mesh particles of the resin. The results shown in Fig. IV-7 indicate that, although the 40 to 60 mesh resin has a high pressure drop with the SX waste, the other mesh size resins have satisfactorily low pressure drops at the flow rate of interest (2 to 4 column volumes per hour). Cesium breakthrough data were then determined for these same mesh sizes of Duolite C-3 resin

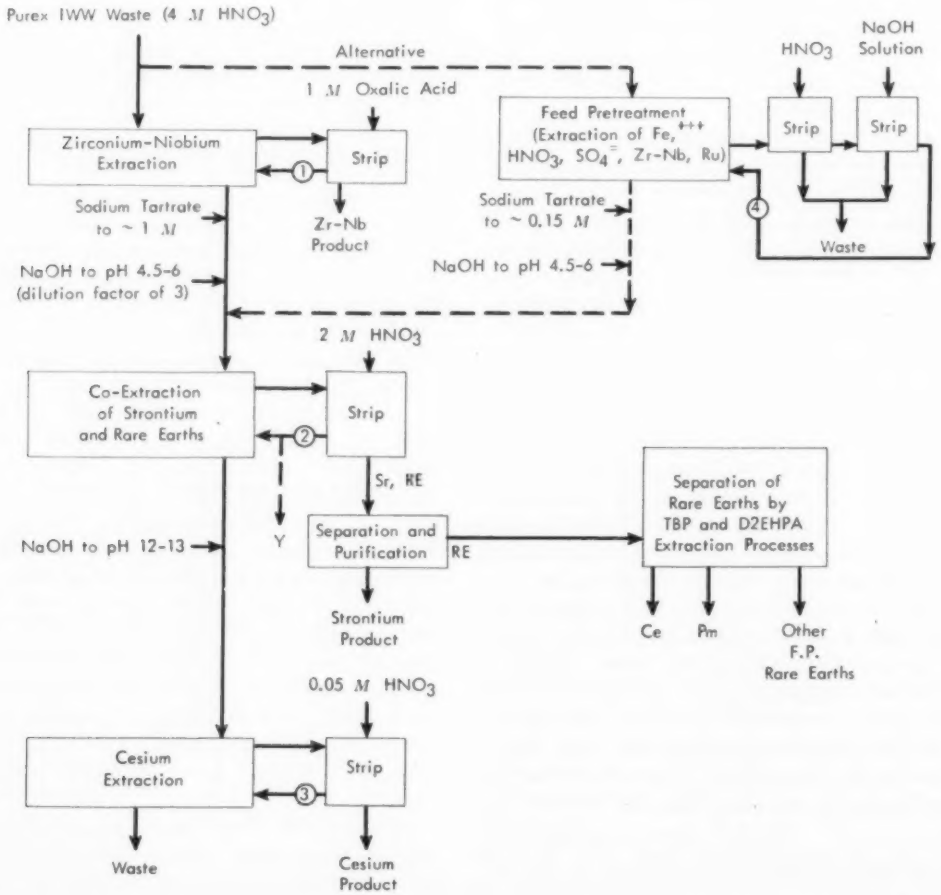

Fig. IV-6 Integrated flow sheet for recovery of fission products.[17] Solvent: (1) 0.3*M* D2EHPA–0.15*M* TBP in Amsco 125-82; (2) 0.2*M* D2EHPA–0.1*M* NaD2EHP–0.15*M* TBP in Amsco 125-82; (3) 1*M* BAMBP in Amsco 125-82; (4) 0.25*M* Primene JM in Amsco 125-82.

and simulated alkaline supernatant waste. These data indicate that, whereas the kinetics of cation exchange are not satisfactory for the 20- to 40-mesh resin, they are satisfactory for the other particle sizes. Therefore the use of 20- to 60-mesh Duolite C-3 resin appears to be satisfactory from the standpoints of low pressure drop and reaction kinetics.

The development of the processes that lead to the recovery and purification of nearly a megacurie of Sr^{90} is presented in detail in a Hanford summary report.[20] Precipitation, solvent extraction, and ion-exchange techniques were involved in this recovery program, which

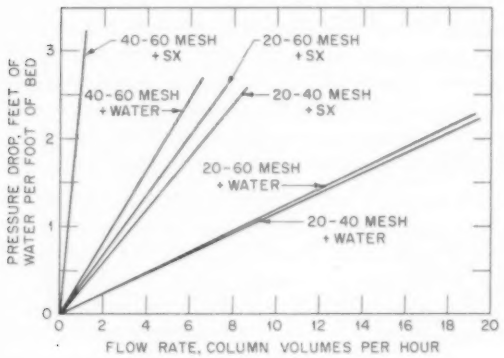
PRESSURE DROP, FEET OF WATER PER FOOT OF BED
FLOW RATE, COLUMN VOLUMES PER HOUR
40-60 MESH + SX
20-60 MESH + SX
40-60 MESH + WATER
20-40 MESH + SX
20-60 MESH + WATER
20-40 MESH + WATER
0
1
2
3
0 2 4 6 8 10 12 14 16 18 20

Fig. IV-7 Pressure-drop data for columns of Duolite C-3 resin with water and with synthetic Redox alkaline supernatant (SX) waste.[3]

provided the Sr^{90} utilized as power sources for thermoelectric power units developed for AEC by the Martin Company. The work described in this report has been extensively reported in previous Reviews.[21]

Wheelwright and Roberts[22] at Hanford have summarized the developmental work of an ion-exchange process suitable for the kilogram-scale production of high-purity promethium.[21] This process was successfully demonstrated in the High-Level Radiochemical Facility at Hanford in which a multicolumn ion-exchange unit was used to recover some 20,000 curies of Pm^{147} from a mixture of rare-earth fission products (cerium was previously removed). The resin used was Dowex 50W-X8 (50 to 100 mesh); the rare earths were eluted at 60°C with a solution of EDTA buffered with ammonium hydroxide. A radiochemical purity for Pm^{147} of greater than 99% (the only contaminants were trace quantities of neodymium and samarium) was achieved for about 13,000 curies of the promethium recovered. A second fraction was composed of 88% promethium (3100 curies), 1% samarium, and 11% neodymium. A third fraction was composed of 55% promethium (4600 curies), 24% samarium, and 21% neodymium.

Corrosion in Waste Processing

At ORNL, corrosion tests of stainless steels (types 304L and 347) have been carried out to determine their applicability as construction materials for tanks to store, on a long-term basis, the acid wastes from the processing of stainless-steel fuel elements.[23]

Specimens of types 304L and 347 stainless steels were exposed in the solution and vapor phases of simulated wastes from the solvent extraction (Purex process) of uranium from the Darex (stainless-steel–UO_2 fuel) and Darex-Thorex (stainless-steel-clad UO_2-ThO_2 fuel) dissolution processes (Table IV-4). No simulation of fission products was attempted. Corrosion specimens of type 304L stainless steel were welded with type 308L weld rod; those of type 347 were welded with type 347 weld rod. No heat-treatment was given the specimens after welding. In some, but not all cases, weld beads were ground smooth before exposure. The effect of this grinding on the corrosion rate appeared to be primarily one associated with a decrease in the surface area of the specimen. Exposures were made at temperatures of 50, 65, and 80°C in both waste solutions and at 43 and 35°C in Darex solutions containing 2*M* free acid. The simulated waste solutions were not renewed during testing since there would be no renewal during storage.

Table IV-4 COMPOSITIONS OF DAREX-PUREX AND DAREX-THOREX WASTE SOLUTIONS[23]

Component	Concentration, moles/liter	
	Darex-Purex	Darex-Thorex
H^+	2–5	1.13
Stainless steel (304L)	1.82	1.82
Al^{3+}		0.28
Cl^-	0.003 (100 ppm)	0.003 (100 ppm)
F^-		0.036–0.04
NO_3^-	To balance	To balance

The results of these corrosion tests indicate that stainless-steel tanks appear to be useful for long-term containment of acid wastes from the processing of stainless-steel fuel elements, provided that the temperature of the container is kept below 50°C and that tanks are constructed so as not to expose grain ends to the solution.

Chloride ions up to about 0.02*M* and fluoride up to about 0.04*M* produced no accelerating effect on the corrosion. Certain organic compounds, e.g., glycerol, acted as corrosion inhibitors, as did nitrate. Ferric iron in high concentrations was responsible for a grain-boundary attack that increased in rate with increase in temperature and with increase in free acid concentration. Catastrophic end-grain attack was observed under the most aggressive conditions. In the usual case, true intergranular attack did not develop even after exposure times of 7000 hr. The presence of Cr(III) appeared to accelerate the attack, but only when Fe(III) was also present. Polarization studies indicated that neither anodic nor cathodic protection would be markedly helpful. Appreciable concentrations of Cr(VI) were shown to be absent from the solution at temperatures as high as 80°C. Radiolysis of these solutions is expected to produce corrosion inhibitors (e.g., NO, NO_2, and H_2O_2) rather than accelerators. Tanks should be open to the atmosphere to ensure that the air in them does not become depleted in oxygen. The effect of fission products (e.g., ruthenium) was not determined.

Corrosion tests[14] of various construction materials are being carried out at ORNL to determine their suitability for use in natural salt at elevated temperatures. A sodium chloride–moist air atmosphere or sodium chloride in the presence of moisture at a high temperature is very severe in its effects on most construction materials. Construction materials being tested include stainless steel (types 304L and 310), Hastelloy C, Haynes 25 alloy, titanium, and

Table IV-5 CORROSION IN SALT[14] AT 300°C

(Exposure Time: 720 Hr)

Medium	Penetration, mils/year					
	Type 304L stainless steel	Type 310 stainless steel	Hastelloy C	Haynes 25 alloy	Titanium 45A	Carbon steel
Natural NaCl	0.4	0.2*	0.1	0.1	0	2.0*
Reagent-grade NaCl	0.2	0.1	<0.1	0.1	0	1.6*
99.5% NaCl–0.5% H_2O	0.5*	0.3*	0.1	0.1*	0.1	1.5*
99.75% NaCl–0.25% $MgCl_2$	0.8	0.4*	0.1	0.2	0.1	3.5*
95% NaCl–5% $CaSO_4$	0.6*	0.2*	0.1	0.1*	0	1.9*
94.25% NaCl–0.5% H_2O–0.25% $MgCl_2$–5% $CaSO_4$	0.4	0.3	0.1	0.1*	0.1	3.8*

*Pitting attack.

Table IV-6 CORROSION IN SALT[14] AT 500°C

(Exposure Time: 720 Hr)

Medium	Penetration, mils/year			
	Type 304L stainless steel	Type 310 stainless steel	Hostelloy C	Haynes 25 alloy
Natural NaCl	0.5	0.1	0.1	0.2
Reagent grade NaCl	0.3	0.5*	0.1	0.1
99.5% NaCl–0.5% H_2O	0.6	0.4	0	0.1
99.75% NaCl–0.25% $MgCl_2$	0.5	0.4*	0.5	0.3
95% NaCl–5% $CaSO_4$	0.4*	0.3*	<0.1	0.1
94.25% NaCl–0.5% H_2O–0.25% $MgCl_2$–5% $CaSO_4$	0.7	0.2	0.1	0.1

*Pitting attack.

carbon steel. The test environment consists of ground natural salt (or reagent salt plus contaminants present in Kansas rock salt) in air and contained in sealed quartz tubes. The quartz tubes, containing the welded coupons and ground reagents in air, were placed in a furnace maintained at the test temperature. Tables IV-5 and IV-6 present the results of corrosion tests at 300 and 500°C, for sample exposure times of 720 hr. Titanium and carbon steel were eliminated from the 500°C tests because rapid attack was observed in earlier, aborted tests.

The data presented in these tables show that in natural salt all the materials (types 304L and 310 stainless steel, Hastelloy C, and Haynes 25 alloy) exhibit satisfactorily low corrosion rates at 500°C. At 300°C the type 310 stainless steel and the carbon steel have low corrosion rates but show pitting. On the basis of these data, type 304L stainless steel will be the most economical and satisfactory material for use in natural salt at both 300 and 500°C. Although Hastelloy C, Haynes 25 alloy, and titanium would also be satisfactory at 300°C, they are more expensive and more difficult to fabricate. Because of the unpredictable nature of pitting corrosion, any material that develops pits is considered unsuitable. (P. Fineman)

References

1. J. M. Skarpelos, Progress in Treatment of a Radioactive Condensate Waste, USAEC Report HW-79174, Hanford Atomic Products Operation, October 1963.
2. *Reactor Fuel Process.*, 7(1): 54 (Winter 1963–1964).
3. E. R. Irish (Ed.), Research and Development Activities, Fixation of Radioactive Residues, Quarterly Progress Report, July–September 1963, USAEC Report HW-79140, Hanford Atomic Products Operation, October 1963.
4. M. W. Wilding and D. W. Rhodes, Removal of Radioisotopes from Solution by Earth Materials from Eastern Idaho, USAEC Report IDO-14624, Phillips Petroleum Co., Nov. 8, 1963.
5. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, February–April 1963, USAEC Report ORNL-TM-603, Oak Ridge National Laboratory, Dec. 16, 1963.
6. Oak Ridge National Laboratory, Chemical Technology Division Annual Progress Report for Period Ending May 31, 1963, USAEC Report ORNL-3452, Sept. 20, 1963.
7. Oak Ridge National Laboratory, Chemical Technology Division Annual Progress Report for Period Ending June 30, 1962, USAEC Report ORNL-3314, Sept. 21, 1962.
8. *Reactor Fuel Process.*, 7(1): 59 (Winter 1963–1964).
9. E. R. Irish (Ed.), Research and Development Activities, Fixation of Radioactive Residues, Quarterly Progress Report, January–March 1963, USAEC Report HW-77299, Hanford Atomic Products Operation, April 1963.
10. *Reactor Fuel Process.*, 7(1): 62 (Winter 1963–1964).
11. *Reactor Fuel Process.*, 6(4): 45 (Fall 1963).
12. J. J. Perona, R. L. Bradshaw, and J. O. Blomeke, Comparative Costs for Final Disposal of Radioactive Solids in Concrete Vaults, Granite, and Salt Formations, USAEC Report ORNL-TM-664, Oak Ridge National Laboratory, Oct. 23, 1963.
13. *Reactor Fuel Process.*, 6(2): 53 (April 1963).
14. Oak Ridge National Laboratory, Health Physics Division Annual Progress Report for Period Ending June 30, 1963, USAEC Report ORNL-3492, Sept. 30, 1963.
15. L. M. Epstein, Formation of Chemically Free Halogen by Radiolysis of Solid Potassium Chloride, USAEC Report WERL-0100, Westinghouse Electric Corp., Pittsburgh, June 1962.
16. *Reactor Fuel Process.*, 6(4): 47 (Fall 1963).
17. D. E. Horner, K. B. Brown, D. J. Crouse, and B. Weaver, Recovery of Fission Products from Waste Solutions by Solvent Extraction, USAEC Report ORNL-3518, Oak Ridge National Laboratory, Dec. 9, 1963.
18. *Nucl. Sci. Eng.*, 17(2): 234-246 (October 1963).
19. *Reactor Fuel Process.*, 7(1): 67 (Winter 1963–1964).
20. Hanford Atomic Products Operation, Hot Semiworks Strontium-90 Recovery Program, USAEC Report HW-72666, July 17, 1963.
21. *Reactor Fuel Process.*, 5(3): 58 (July 1962).
22. E. J. Wheelwright and F. P. Roberts, Development and Demonstration of an Ion-Exchange Process for Kilogram-Scale Production of High-Purity Promethium, USAEC Report HW-78651(Rev.), Hanford Atomic Products Operation, October 1963.
23. D. N. Hess, L. Rice, B. Willis, E. S. Snavely, and W. E. Clark, Corrosion of Stainless Steel in Acidic Nitrate Waste Solutions from Processing Stainless Steel Reactor Fuels, USAEC Report ORNL-3474. Oak Ridge National Laboratory, Oct. 16, 1963.

Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Recovery of Uranium from Ores

The Australian Atomic Energy Commission has published a collection of articles on the development of the uranium mining industry in Australia.[1] The pamphlet includes descriptions of the metallurgical operations employed in the production of uranium concentrates at Rum Jungle, Mary Kathleen, Radium Hill, and Port Pirie facilities. The mine at Radium Hill and the chemical treatment plant at Port Pirie have been closed by the South Australian Government in view of diminishing reserves of ore and the absence of a market for uranium concentrates.

Gautier[2] has described the procedures used in producing uranium concentrates at the Forez Plant of the Societe Industrielle des Minerais de l'Ouest in France. At Forez the uranium ore is leached with dilute sulfuric acid in the presence of a chloride oxidizing agent. The uranium concentrate is obtained by a two-step precipitation process. During the first stage the excess acid in the leach solution is precipitated in the form of calcium sulfate and ferric sulfate. In the second stage a uranium concentrate is produced by coprecipitation of uranium and aluminum sulfates. The uranium-bearing precipitate is dissolved in a calcium nitrate solution. The solution is acidified with nitric acid, and the uranium is recovered in purified form by conventional solvent-extraction techniques.

A process for obtaining uranium oxide directly from ores has been described by Kangro.[3] The process depends on the separation of elements by the selective volatilization of their chlorides. The initial step in the process involves the reaction between the ore and chlorine gas at 750°C to remove lead and vanadium as volatile $PbCl_2$ and $VOCl_3$, respectively. The ore is then purged with air for a short period. Uranium is recovered from the ore by chlorination with chlorine gas at 1050 to 1100°C. At this temperature uranyl chloride (UO_2Cl_2) is volatile and is removed from the ore gangue in the process gas stream along with volatile ferric chloride and titanium tetrachloride. Uranium oxide is recovered by oxidation of uranyl chloride at 450°C. Approximately 95% recovery of uranium has been demonstrated in laboratory tests.

A book devoted to the metallurgy of uranium has recently been published.[4] Approximately one-third of the text is devoted to the operations employed in the production of uranium metal from ores. The remainder of the text covers the physical metallurgy of uranium metal and alloys.

Production of Uranium Oxides

Uranium Oxide from Uranyl Nitrate Solutions

Uranium trioxide is an important intermediate in the commercial production of uranium dioxide and uranium tetrafluoride. The oxide is prepared commercially by calcination of uranyl nitrate solutions. Otero[5] has described a pilot-plant facility, operated by Junta de Energia Nuclear (JEN) in Spain, in which a process for the calcination of uranyl nitrate solutions at a temperature of 300 to 350°C using fluidized-bed techniques has been demonstrated. By this process, uranium trioxide particles with diameters between 80 and 400 μ are produced. Workers at JEN have also used fluidized-bed techniques in the production of uranium tetrafluoride from uranium dioxide.[6]

Although the thermal decomposition of uranyl nitrate hexahydrate (UNH) is an important step in the production of uranium trioxide, many uncertainties exist in the process performance owing to the lack of information on the decomposition of UNH. Ondrejcin[7] has investigated the mechanism of decomposition and the kinetics at temperatures up to 400°C. The data for the thermal decomposition under vacuum and at atmospheric pressure do not follow simple kinetics. The decomposition appears to be a combination of reactions of several different orders with changing mechanisms. Under vacuum at 250 to 300°C, the first half of the denitration follows a zero-order reaction. At 350 and 400°C the first three-fourths of the UNH decomposes by zero-order reaction. The thermal decomposition of UNH may be described as a heterogeneous autocatalytic reaction. The point at which the denitration reduction ceases to follow zero-order kinetics also corresponds to the point at which 90 to 95% of the water initially present is vaporized. At this point the reaction rate decreases markedly, showing that the first part of the reaction is autocatalytic with respect to water or nitric acid but not oxides of nitrogen. The reaction rates toward the end of this reaction are evidently fixed by diffusion control of the reaction as a limiting step. A comparison of data obtained under vacuum and at atmospheric pressure indicates that the mechanisms of reaction are similar, but not the same, and are pressure dependent.

A continuous process has been developed at Mallinckrodt Chemical Works for the direct conversion of uranyl nitrate solutions to uranium dioxide.[8] The concept involves atomizing aqueous uranyl nitrate directly into a reducing flame of propane gas. Propane, air, and uranyl nitrate are introduced into the reactor through a burner-nozzle assembly. The reactor temperature, which is normally at least 980°C at the exit end, is controlled by the uranyl nitrate flow and by excess hydrocarbon introduced around the spray nozzle. The major problems encountered in pilot-plant tests were the continuous formation of heavy deposits of dry powder on the walls of the reactor and the difficulty in producing high-assay (>97%) uranium dioxide product. Powder buildup on the reactor wall resulted from extremely low gas velocity at the wall. Insertion of a Venturi-shaped liner in the reactor greatly reduced the powder deposits on the walls, whereas the residence time of oxide in the reactor was not decreased. Conversions to 82% UO_2 have been achieved at production rates of 242 lb of uranium per hour on a pilot-plant scale, whereas products assaying 96% UO_2 have been produced in the laboratory. The product is a finely divided low-density powder with an average particle size of from 2.0 to 5.5 μ. In general, the product was more reactive to hydrogen fluoride than oxides produced by other processes. Additional development work is needed to optimize the processing variables in order to provide at least 97% conversion to UO_2 which is required for the production of high-grade uranium metal.

Electrolytic Reduction of Uranyl Chloride

The process of electrodepositing coarse crystalline uranium dioxide from a fused-chloride electrolyte has been studied for application to the preparation of crystalline uranium dioxide as a power-reactor fuel. To be suitable for use in a reactor, uranium dioxide should have a large crystal size, high density, and an oxygen-to-uranium ratio of less than 2.015. Scott and Mudge[9] have reported the results of an investigation at Hanford Atomic Products Operation (HAPO) on the preparation of single crystals of UO_2 by electrolytic reduction of uranyl chloride in LiCl-KCl (m.p. 460°C) or 2.5 KCl-$PbCl_2$ (m.p. 580°C). Uranyl chloride was added to the molten salt as the monohydrate or was formed in the melt by the treatment of U_3O_8 or UO_2 with chlorine gas. After dissolution of all solid material, the melt was continuously purged with chlorine or with anhydrous hydrogen chloride to remove all hydroxide and oxide impurities. Whether or not this treatment was complete was determined by the appearance of the UO_2 deposit. A fine dendritic deposit, resulting from the rapid growth of needles on the cathode, was an indication that the oxide and hydroxide removal was incomplete.

Single crystals ranging up to 4 g in weight have been prepared by electrolytic reduction of uranyl chloride.[9] These crystals were grown under the following conditions:

Melt composition	2.5 KCl-$PbCl_2$
Initial uranium concentration	30 wt.%
Deposition potential	−0.5 volt
Melt temperature	500°C
Cell atmosphere	Cl_2 or HCl
Cathode	$^1/_{32}$-in.-diameter Pt ball

The impurity contents of the crystals prepared from 2.5 $KCl-PbCl_2$ melt were K = 50 ppm, Cl = 200 ppm, and Pb = 50 ppm. The density of individual crystals, as measured by liquid displacement, was close to the theoretical value for UO_2. A detailed description of the pilot-plant facilities for producing high-density UO_2 at HAPO was presented in a recent Review.[10]

Stromatt[11] has observed that the reduction of UO_2^{2+} to uranium dioxide in molten KCl-NaCl salt at 716°C is diffusion controlled at a platinum electrode. The reaction occurs in two steps at nearly the same potential. The electrode reaction proceeds by the reduction of UO_2^{2+} to UO_2^+ followed by the reduction of UO_2^+ to solid UO_2. The U(V) species is soluble in the salt, and a stable solution of U(V) was prepared by the reduction of uranyl ions by uranium dioxide.

Scott has reported the results of a series of experiments designed to investigate the feasibility of producing uranium suboxides by electrolytic techniques.[12] The tests were performed using LiCl-KCl melts containing U(IV), and in some tests U(III). It was observed that uranium dioxide was produced by electrolysis from a melt containing only U(IV) or a mixture of U(IV) and U(III). This suggests that some of the U(IV) must exist in the melt as an oxygenated species. In other tests both UO_2 and uranium metal were the products of electrolysis. In no test, however, was a suboxide of uranium identified as a product.

Production of Uranium Carbides and Nitrides

Production of Uranium Carbide

A method has been developed at Harwell for the preparation of uranium monocarbide directly from uranium dioxide using fluidization techniques.[13] The process has been demonstrated on a small scale using batch operation. An intimate mixture of uranium dioxide and graphite is prepared by wet ball milling. The blend is dried, compacted, and crushed to give particles of 30 to 40 mesh. Uranium monocarbide is produced by fluidizing the particles for 4 hr in a stream of argon at a bed temperature of 1500°C. The cone-shaped fluidization apparatus is fabricated of a special graphite, selected for its machinability, good high-temperature characteristics, and susceptibility to radio-frequency heating.

The possibility of synthesizing uranium monocarbide and other refractory compounds of interest as reactor fuels from liquid-metal solutions is currently being investigated at Argonne National Laboratory (ANL).[14,15] Uranium monocarbide is prepared by precipitating with carbon the uranium dissolved in a volatile liquid-metal solvent. A series of tests was made[14] to evaluate the process scheme for application to the production of 500-g batches of carbide. It was observed that, to reduce significantly the oxygen content in the product, the activated charcoal used as the carbon source must be thoroughly degassed. The optimum uranium-to-carbon mole ratio in the charge was 1:1.10. The use of sodium as a wetting agent does not appear to be so effective in enhancing the reaction rate in large-scale experiments as was observed[16] in small-scale studies.

Equipment has been constructed at ANL[15] for the preparation of 500-g batches of uranium monocarbide by precipitation from liquid-metal solution. The process consists of dissolution of uranium metal in zinc-magnesium alloy, addition to the metal solution of degassed activated charcoal, removal of the supernatant liquid metal from the precipitated uranium monocarbide, and retorting of the uranium monocarbide product under vacuum to remove residual zinc and magnesium.

Uranium monocarbide can be prepared by the reaction of magnesium carbide with uranium tetrafluoride dissolved in a flux composed of 35 mole % LiCl and 65 mole % $MgCl_2$ (Ref. 15). Uranium monocarbide precipitated from the solution and was separated by filtration in an inert atmosphere.

Wymer and Dean[17] have investigated the feasibility of a direct gas-phase process for converting uranium hexafluoride to uranium monocarbide. They have shown thermodynamically that the gas-phase reaction of UF_6 with CH_4 and H_2 to form solid UC is approximately 80% complete at 2000°K and 0.01 atm equilibrium pressure. Uranium monocarbide formation appears to be strongly favored under conditions of decreased pressure and increased temperature.

Properties of Uranium Carbides

In attempts to prepare $UC_{2.0}$, Ferris and associates at Oak Ridge National Laboratory

(ORNL)[18] have shown that the maximum combined-carbon-to-uranium ratio is 1.85 ± 0.03. Specimens with higher carbon-to-uranium ratios were binary mixtures of $UC_{1.85}$ and graphite. Therefore uranium dicarbide is actually a carbon deficient compound. The compound $UC_{1.85}$ is thermally stable at temperatures between 1260 and 2000°C.

The heat of formation of uranium dicarbide, $UC_{1.90}$, has been reported by Huber, Head, and Holley[19] from measurements made of its heat of combustion in oxygen. The most accurate value of the heat of formation of $UC_{1.90}$ is $\Delta H_f = 21.1 \pm 1.4$ kcal/mole.

A survey of uranium carbides, nitrides, and silicides has appeared in a recent issue of *Atomic Energy Review*.[20] This article discusses the chemical, physical, and mechanical properties of these compounds, as well as techniques for preparing them. Mukaibo and Naito[21] have reviewed the thermochemical properties of uranium carbides with special intent to develop equations for UC and UC_2 relating specific heats to temperature. From these equations the heats of formation, free energies of formation, and entropies of formation were calculated as a function of temperature.

Uranium Nitride

Uranium nitride has many favorable characteristics that make it potentially attractive as a nuclear fuel. In powder form it is not nearly so reactive with the atmosphere as uranium monocarbide. Because of the high uranium content of UN, it can be substituted for UO_2 in a dispersion fuel element and occupy approximately 30% less volume at an equivalent uranium content. Evans and Davies[22] have reviewed the properties and the methods of preparation of the uranium nitrides. The uranium-nitrogen phase relations have been reported recently.[23] These data are necessary in the application of UN as a fuel material, since they provide the bases for the selection of preparation techniques and for the evaluation of physical, mechanical, and chemical property measurements. From these data (Fig. V-1), the following conclusions can be made:

1. A minimum nitrogen pressure of 2.5 atm is required to produce cast uranium mononitride. At lower pressures it is impossible to saturate the uranium liquid phase to the UN composition.

2. It is possible to produce UN by the decomposition of U_2N_3 at fairly low temperatures in a pumping system that will maintain a reasonable vacuum. However, because the kinetics are extremely slow at lower temperatures, 1000°C is the minimum reasonable temperature for production processes.

3. Below 2.5 atm and below 2850°C, UN decomposes to uranium and nitrogen. At nitrogen

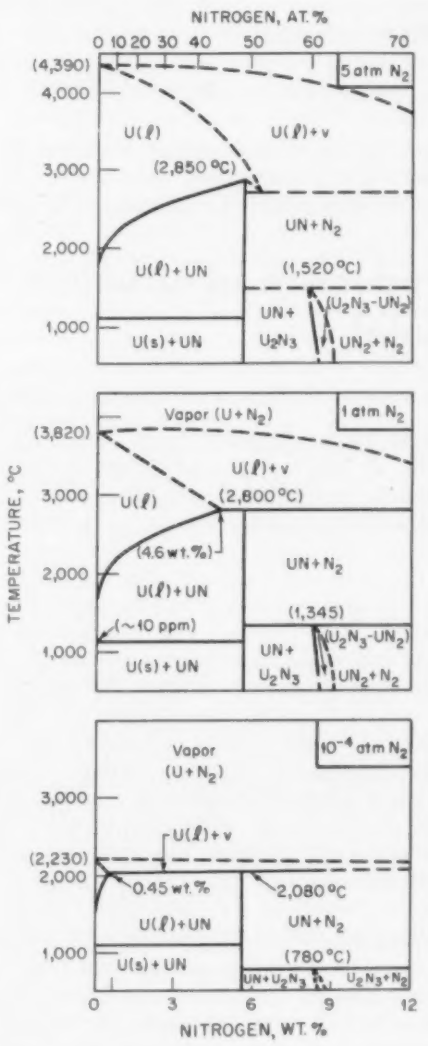

Fig. V-1 Uranium-nitrogen phase diagrams. Reprinted here by permission from *Nucleonics*, 22(1): 64.

pressures above 2.5 atm, UN melts congruently at 2850°C. By comparison, at 1 atm nitrogen pressure, UN decomposes at 2800°C by loss of nitrogen, and the uranium liquid phase that forms contains 4.6 wt.% nitrogen.

Uranium nitride has been prepared at Harwell using fluidized-bed techniques.[13] The preparation involves the blending of uranium dioxide and carbon into pellets which are subsequently fluidized in a stream of nitrogen at 1500°C. The reaction proceeds according to the following equation:

$$UO_2 + 2C + 0.5N_2 = UN + 2CO$$

Strict stoichiometric proportions must be observed within the UO_2-C compact to prevent uranium carbonitride formation.

Production of Uranium Metal

Electrolytic Reduction of Uranium Dioxide

High-quality uranium metal has been produced at Mallinckrodt Chemical Works from uranium dioxide by fused-salt electrolysis.[24] The reduction cell consists of a cylindrical graphite crucible that serves both as the cathode of the cell and as a container for the molten fluoride electrolyte and molten uranium metal product. In previous work,[25] reductions were made with consumable anodes containing a uranium dioxide–carbon mixture. Recent efforts[24] have been directed toward feeding the oxide directly to the electrolytic cell, thus avoiding the cost of preparing the UO_2-carbon anodes. A major problem associated with continuous oxide feed to the cell is oxide contamination of the uranium metal product. This contamination results from the fact that uranium dioxide is only slightly soluble in the electrolyte and also exhibits a low rate of dissolution in the melt.

It was observed in preliminary tests[24] that direct feed of oxide requires a careful balance between feed rate and anode current density. The objective of the tests was to achieve feed rates and current efficiencies as high as possible without contaminating the metal with oxide. Uranium dioxide powder was fed to the cell using a piston type feeder. The current was maintained at a high level to avoid oversaturating the electrolyte with oxide. Three types of graphite anodes were evaluated, and a design incorporating a slotted solid graphite cylinder appeared satisfactory. The main criterion in the design of the anode is to avoid contamination of the electrolyte and metal with UO_2 particles.

The concentration of uranium tetrafluoride in the electrolyte appears to be the most important variable affecting the throughput of a particular-sized cell. It was observed that the throughput and anode current density increases with increasing UF_4 content in the melt. The current efficiency, however, showed little change. The direct dependence of current density on UF_4 concentration may indicate that the solubility of uranium dioxide in the melt increases with increased UF_4 content.

Methods of tapping the molten uranium product from the electrolytic cell and transferring the molten metal to ingot molds have been tested on laboratory and pilot-plant scale.[26] A vacuum-withdrawal system using a heated graphite pipe to carry the molten uranium to an evacuated mold chamber appears feasible and will be evaluated further in a prototype cell.

Workers at the U. S. Bureau of Mines[27] have also produced, on a laboratory scale, high-purity uranium metal by electrolytic reduction of uranium dioxide in fluoride melts at 1200°C. Preliminary tests were performed in which uranium dioxide was added continuously to the cell during electrolysis. The major impurities found in the metal were aluminum, barium, iron, silicon, carbon, and oxygen. The effects of cell design and geometry were investigated; the most important factor in cell performance was the electrode arrangement within the cell.

Carbon Reduction of Uranium Dioxide

Smiley[28] has reported the results of preliminary investigations on the preparation of uranium metal by the carbon reduction of uranium dioxide. The reduction feed is prepared by blending powdered uranium dioxide with carbon and pressing the powdered mixture into pellets with the use of a binder. In the preliminary tests the carbon-to-uranium mole ratio in the pellets ranged from 1.69 to slightly greater than 2. The reductions are carried out in a UO_2 crucible at a temperature of 1800 to 1900°C in a continuously evacuated system. The reduction

proceeds by the formation of uranium oxycarbide that subsequently decomposes to give uranium metal. The carbon content of the metal product ranged from 0.01 to 0.5 wt.%. It was observed that significant uranium losses occurred by evaporation during the reduction. It is expected that uranium loss by this mode would be reduced to an insignificant level by proper design of the reduction cell.

Direct Reduction of Uranium-Ore Concentrates

Owing to the success achieved at ANL in the reduction of uranium oxides by zinc-magnesium alloys in the presence of molten fluxes,[29] a series of tests was performed to evaluate the direct reduction of uranium-ore concentrates to metal in similar systems.[30,31] Production of reactor-grade uranium by this technique would eliminate a series of purification and chemical conversion steps currently in use. Preliminary tests[30] indicated that uranium metal can be prepared from ore concentrate by reduction with zinc–6 wt.% magnesium alloy at 750°C using a flux containing 47.5 mole % $MgCl_2$–47.5 mole % $CaCl_2$–5 mole % MgF_2. The tests showed that silicon, which is present in the ore concentrate to the extent of 1.1 wt.%, is coreduced with the uranium. Several methods were studied for removing silicon from the ore concentrate in a pretreatment step. The most convenient and effective method appeared to be the volatilization of silicon by treatment of the ore concentrate with ammonium bifluoride for 4 hr at 145°C (Ref. 31). Approximately 90% of the silicon is volatilized using an ammonium bifluoride-to-ore concentrate weight ratio of 0.15.

The process steps in the reduction of uranium-ore concentrates have been established[31] as (1) pretreatment of the concentrate with ammonium bifluoride to remove silica, (2) chlorination of the concentrate to remove certain gangue elements (chlorine is generated by exposure of the magnesium chloride–magnesium fluoride flux to air), (3) reduction of uranium by zinc–5 wt.% magnesium alloy under an argon atmosphere, (4) retorting of the metal under vacuum to remove zinc and magnesium from the uranium product, and (5) arc melting of the uranium to produce a consolidated product. This procedure has been employed in laboratory tests with the production of good quality metal in yields of greater than 95%.

Recovery of Uranium from Refinery Wastes

At the Atomic Energy Commission Feed Materials Production Center, Fernald, Ohio (operated by National Lead Co. of Ohio, NLCO), purified uranium trioxide is converted to uranium tetrafluoride, which is subsequently reduced to massive metal. Uranium metal is fabricated into fuel cores for use in plutonium production reactors. Each process step generates uranium-bearing residues that must be processed for uranium recovery either by direct remelting or by hydrometallurgical techniques.[32] The residues may be conveniently considered as high grade or low grade according to the uranium content and subsequent handling.

High-grade residues include massive metal pieces not suitable for remelting, chips and turnings from metal fabrication operations, and black oxide (U_3O_8). Massive metal pieces are processed through a hydrochloric acid metal dissolver to produce a solution of uranous chloride. Finely divided metallic residues are burned in a rabble-arm type furnace to uranium oxide, U_3O_8.

Low-grade residues consist primarily of magnesium fluoride slag generated in the reduction of UF_4 with magnesium. Also included in these residues are dust-collector residues, floor sweepings, and sump cakes. The residues are calcined, ground, and reduced to a 60% slurry in water. The slurry is used as a feed material for a recovery process based on a HCl leach and precipitation of uranium as uranyl ammonium phosphate (UAP). The flow sheet for the UAP process is shown in Fig. V-2. The feed slurry is dissolved in hydrochloric acid containing MnO_2 as an oxidant. The acid slurry is filtered, and the uranium content of the filtrate is precipitated as $UO_2NH_4PO_4$ (UAP) by the addition of ammonia and phosphoric acid. The UAP cake is filtered and calcined to remove ammonia and fluoride.

The process provides a good separation from most contaminants. Ferric iron, however, is coprecipitated with uranium. Therefore it is necessary to reduce the iron to the ferrous state prior to uranium precipitation. Sodium thiosulfate has been employed as a reducing agent;[32] however, recently, laboratory tests[33] have shown that uranous (U^{4+}) chloride solutions can be substituted for sodium thiosulfate.

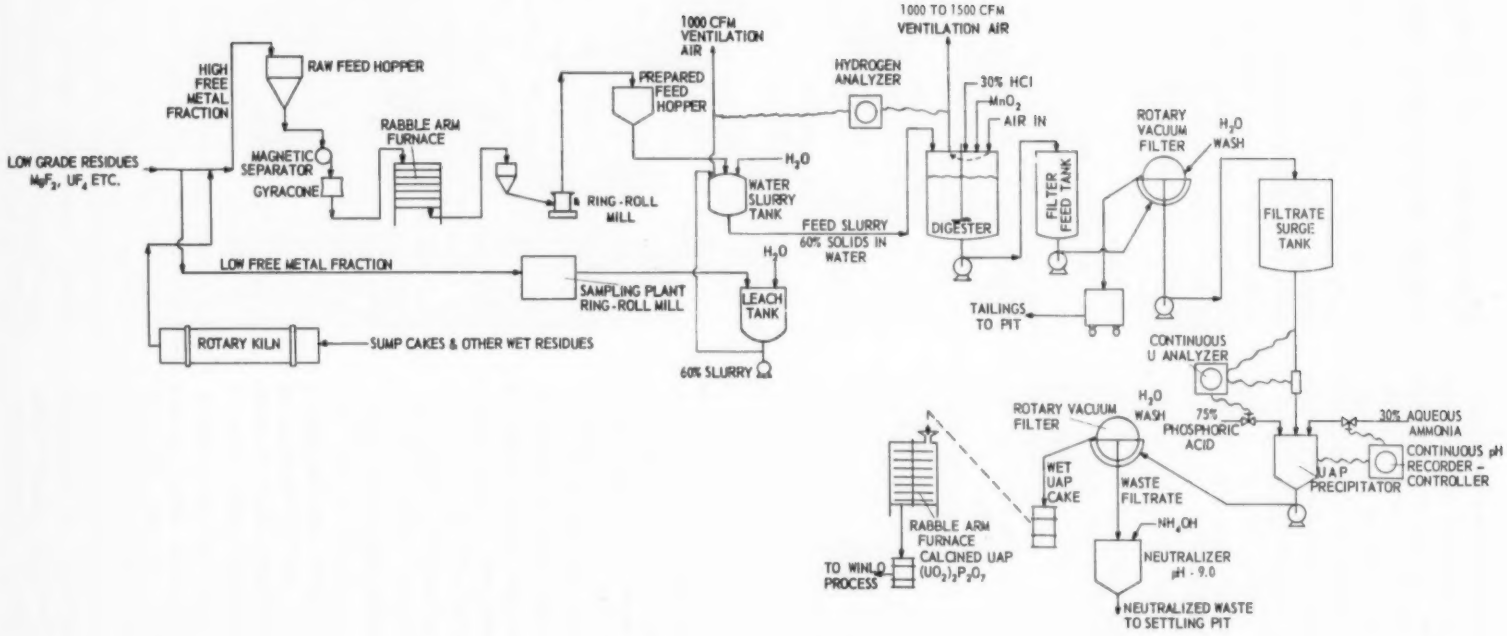

Fig. V-2 Recovery of uranium from low-grade residues as uranyl ammonium phosphate (UAP).

A cost savings of $0.155 to $0.269 per pound of iron reduced is expected from the use of uranous chloride instead of sodium thiosulfate. Uranous chloride is available in the uranium recovery plant from the hydrochloric acid metal dissolver.

Recently, a large-scale uranium tetrafluoride aqueous precipitation production unit (Winlo process) was put on stream at NLCO for the recovery of uranium from scrap materials.[32]

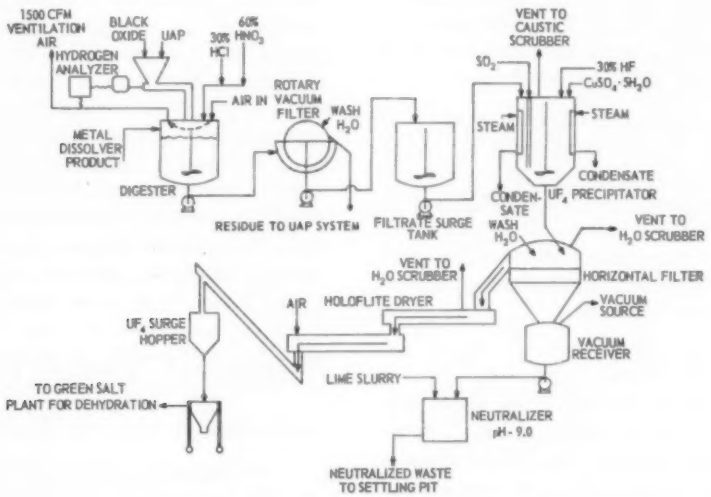

Fig. V-3 Winlo system for producing uranium tetrafluoride.

The flow sheet is shown schematically in Fig. V-3. As indicated, the feed for the Winlo process may consist of black oxide produced in the high-grade feed preparation system, calcined UAP cake, and uranous chloride solution produced in the metal dissolver. The digestion of solid feed is conducted in batches. First, the estimated requirement of hydrochloric acid and nitric acid (as an oxidant) is pumped into the digester. The solids are added by a screw feeder at the maximum rate consistent with low foaming in the digester and maintenance of a hydrogen concentration of 1.0% or less in the off-gas stream. A leach time of 3 hr is allowed at a temperature of 70°C. The proportion of solid feed and acid to the digestion is adjusted to produce a liquor assaying 225 g of uranium per liter and containing 1.2*N* excess acid.

The uranium solution is prepared for UF_4 precipitation by adding hydrofluoric acid and cupric sulfate to the liquor and raising the temperature of the solution to 90°C. Aqueous HF is added in sufficient quantities to provide an excess of 12 to 15 g/liter. When UAP is being processed, the excess is raised to 40 g of HF per liter to minimize phosphate contamination of the product. Sufficient $CuSO_4 \cdot 5H_2O$ is added to the liquor to produce a cupric ion concentration of 5 g/liter. Uranium is precipitated as $UF_4 \cdot \frac{3}{4}H_2O$ by bubbling sulfur dioxide gas into the hot solution. The reactions involved in the precipitation step can be represented by the following equations:

$$2CuCl_2^{2-} + SO_2 + 2H_2O \rightarrow 2CuCl_2^{-} + SO_4^{2-} + 4H^+ + 4Cl^-$$

$$2CuCl_2^{-} + 4HF + UO_2^{2+} + 4Cl^- \rightarrow \underline{UF_4} + 2CuCl_2^{2-} + 2H_2O$$

$$UO_2^{2+} + SO_2 + 4HF \rightarrow \underline{UF_4} + SO_4^{2-} + 4H^+$$

The reduction of hexavalent uranium to tetravalent uranium is accomplished by the catalytic action of the cuprous chloride ion, which is continuously regenerated from the cupric chloride ion by the addition of sulfur dioxide during the precipitation step. Sulfur dioxide will not reduce U(VI) to U(IV) directly. The uranium tetrafluoride product is a high-density (3 g/cm^3) material that is easily filtered.

It has been found in both laboratory tests and plant operation that the major variables affect-

ing the character of the UF_4 product are the operating temperature and the concentration of certain impurities.[32] A temperature of 88 to 91°C has been selected as the optimum for the precipitation step. As the temperature is decreased from this value, the uranium tetrafluoride hydrate progressively retains more water until a $UF_4 \cdot 2.5H_2O$ product is formed at ambient temperature. Also, the product becomes progressively less dense, possesses undesirable filtration properties, and has less desirable characteristics for subsequent metal production. At temperatures above 91°C the solubility of SO_2 decreases markedly so that a practical reaction rate is not maintained.

The presence of appreciable concentration of alkali or alkaline-earth metals in the feed solution affects the nature of the UF_4 product in that these metal ions form insoluble double fluoride salts with uranium. High concentrations of free acid, sulfate, and phosphate decrease the reduction reaction rate probably because of an adverse effect on SO_2 solubility.

Plant operating experience at NLCO has shown that the UAP process should be replaced as a means of producing feed to the Winlo process since a more direct route, specifically designed to produce feed for the Winlo process, would reduce feed preparation costs markedly.[34] Also, it has been observed that some low-grade residues containing slightly enriched uranium cannot be converted to UAP of sufficient purity for Winlo feed and a large fraction of this material must be recycled. Recent plant experience has revealed that UF_4 produced from calcined UAP by the Winlo process contains 100 to 300 ppm phosphorus which carries through to the metal. Although the effect of this amount of phosphorus on metal quality is unknown, it has been considered best to eliminate this contaminant.

Both ion-exchange and solvent-extraction systems are being evaluated[34] as a means for producing feed for the Winlo process from low-grade uranium residues. A Higgins semicontinuous ion-exchange column was used for the production of pure uranyl chloride solutions from scrap leach liquors. Laboratory solvent-extraction tests demonstrated that a 20 wt.% Aliquat 336–80 wt.% Solvesso-100 system will satisfactorily extract uranium from a hydrochloric acid leach liquor produced by the digestion of low-grade residues.

The use of the UAP-Winlo route has led to the problem that a small amount of phosphate, apparently coprecipitated with the UF_4, was retained during the dehydration operation and was subsequently converted to uranium phosphide in the reduction to metal. The Winlo green salt hydrate ($UF_4 \cdot \frac{3}{4}H_2O$) prepared from UAP feed contains approximately 250 to 300 ppm phosphorus. A tentative specification has been established limiting the amount of phosphorus in the uranium metal to a maximum of 35 ppm. A series of plant-scale tests was performed to determine the extent of phosphorus removal during the dehydration of Winlo green salt in a hydrogen fluoride atmosphere.[35] It was concluded that in routine operation an overall phosphorus decontamination factor of about 3 can be attained by hydrogen fluoride dehydration at 595°C. The proper blending of product lots apparently permits dehydrated green salt containing less than 35 ppm phosphorus to be produced from feed containing as much as 300 ppm phosphorus.

Thorium-Metal Production

Reduction of Thorium Dioxide

A development program has been under way at ANL to evaluate the reduction of thorium dioxide by zinc-magnesium alloys in the presence of molten fluxes.[15,36–39] The range of flux composition in which satisfactory reduction takes place with $CaCl_2$-$MgCl_2$-CaF_2 fluxes is greatly increased by the use of an inert atmosphere. At the optimum fluoride anion concentration of 10 at.% in the flux and with sufficient ThO_2 present to give a 1% alloy, only 10 or 11 at.% magnesium cation is needed to achieve complete reduction in an inert atmosphere, whereas over 50 at.% magnesium cation is required for complete reduction in an air atmosphere.[37] An increase of the thorium loading in the final metal phase from 1.0 to 9.1 wt.% requires that the magnesium chloride concentration in the flux be raised from 10 to 15 mole % to 50 mole % to achieve complete thorium reduction.[38] The other flux constituents are 10 mole % CaF_2 and 40 mole % $CaCl_2$. It appears that the rate and extent of thorium dioxide reduction are highly dependent on the magnesium metal concentration in the zinc phase, reaching a maximum between 5 and 10 wt.% magnesium. Efficient mixing is required to achieve satisfactory reduction rates.

The most satisfactory processing conditions on a laboratory scale are:[38]

Reduction temperature	800°C
Mixing rate	800 rpm
Atmosphere	Argon
Final magnesium concentration in metal phase	10 wt.%
Flux composition	47.5 to 50 mole % $MgCl_2$; 5 to 10 mole % CaF_2; balance $CaCl_2$
Reduction time	4 hr
Pouring temperature	850°C

Recent work[39] has shown that, by the use of a flux containing only magnesium, it has been possible to extend the range of magnesium metal concentration in the zinc phase over which complete reduction of thorium dioxide occurs. The use of a flux containing 90 mole % $MgCl_2$ and 10 mole % MgF_2 yielded nearly complete ThO_2 reduction over a range of magnesium concentration in the metal phase from 5 to 15 wt.%. Further studies[15] have indicated that a ThO_2 to flux weight ratio of less than 0.2 is required for complete reduction using a flux containing only magnesium cation.

Reduction of Thorium Tetrachloride

Workers at Ames Laboratory[40] are developing a process for producing high-purity thorium metal by the reduction of thorium tetrachloride with magnesium. Thorium tetrachloride is mixed with sufficient magnesium to reduce $ThCl_4$ and to form a thorium–20 wt.% magnesium alloy. Reductions were accomplished by heating the charge (4.4 kg of $ThCl_4$, 1.25 kg of Mg) in a tantalum crucible under an inert atmosphere for 1 hr at 965°C and for 20 min at 1025°C. The crucible was cooled to room temperature, and the $MgCl_2$ slag was removed from the alloy. As an average, 3.2 kg of thorium–20 wt.% magnesium alloy was obtained, which corresponds to 94% yield of thorium metal. The alloy was crushed and heated under a prescribed schedule to 920°C *in vacuo* to remove the magnesium and residual. A stepwise heating cycle was used during the magnesium removal operation to avoid melting of the alloy. The final thorium sponge was consolidated by nonconsumable arc melting.

The thorium tetrachloride employed in the reduction studies was prepared by the chlorination of thorium dioxide with chlorine in the presence of graphite powder.[40] Purification of the tetrachloride was effected by multiple sublimation under reduced pressure. Since this purification procedure is rather complex, considerable interest has developed in the reaction of phosgene with thorium dioxide as a means for producing thorium tetrachloride.[40] The reaction between dissociated phosgene and ThO_2 has been found to proceed by two steps at 600°C with the initial step being the production of $ThOCl_2$ as an intermediate. The first reaction, $ThO_2 + CO + Cl_2 \rightarrow ThOCl_2 + CO_2$, goes nearly to completion, and the equilibrium constant appears to be greater than 10,000. The second reaction, $ThOCl_2 + CO + Cl_2 \rightarrow ThCl_4 + CO_2$, appears to have an equilibrium constant of approximately 1000. These large equilibrium constants indicate that very efficient usage of phosgene could be achieved in this reaction.

(J. J. Barghusen)

References

1. *Uranium in Australia*, The Australian Atomic Energy Commission, Sidney, Australia, 1962.
2. R. Gautier, Chemical Concentration of Uranium Ores, *Energie Nucl.*, 4: 600–606 (1962); also in USAEC Translation AEC-tr-6020.
3. W. Kangro, Obtaining Heavy Metals Especially Uranium from Poor Ores by Means of Gaseous Chlorine II, *Z. Erzbergbau Metallhuettenw.*, 16(7): 328–333 (July 1963).
4. J. H. Gittus, *Uranium*, Butterworth, Washington, 1963.
5. A. R. Otero, Description of an Installation for Obtaining Uranium Trioxide by Calcination of Uranyl Nitrate Solution in a Fluidized Bed, *Energia Nucl. (Madrid)*, 7(26): 4–14 (April–June 1963).
6. E. C. Lago and A. R. Otero, Obtaining Uranium Tetrafluoride in a Fluidized Bed Reactor, *Energia Nucl. (Madrid)*, 7(27): 21–29 (July–September 1963).
7. R. S. Ondrejcin, Thermal Decomposition of Uranyl Nitrate Hexahydrate, USAEC Report TID-17733, Savannah River Laboratory, January 1963 (submitted to *J. Chem. Eng. Data*).
8. W. H. Hedley, R. J. Roehrs, and W. T. Trask, Jr., Production of Uranium Dioxide by Flame Denitration, *Ind. Eng. Chem., Process Design Develop.*, 3(1): 11–14 (January 1964).
9. F. A. Scott and L. K. Mudge, The Electrolytic Preparation of Single Crystals of Uranium Dioxide, *J. Nucl. Mater.*, 9(3): 245–251 (1963).
10. *Reactor Fuel Process.*, 6(3): 49–52 (July 1963).
11. R. W. Stromatt, Studies on the Electroreduction

of Uranyl(VI) in Molten Equimolar KCl-NaCl by Chronopotentiometric and Electrode Impedance Measurements, *J. Electrochem. Soc.*, 110(12): 1277-1282 (December 1963).

12. F. A. Scott, Experiments on the Preparation of Uranium Suboxides by Electrolytic Deposition, USAEC Report HW-76873, Hanford Atomic Products Operation, Mar. 5, 1963.
13. A Direct Path from Refractory Oxides to Carbides, *Chem. Eng.*, 70(23): 134, 136 (Nov. 11, 1963).
14. Argonne National Laboratory, Chemical Engineering Division Summary Report, April–June 1962, USAEC Report ANL-6569, pp. 63-65, August 1962.
15. Argonne National Laboratory, Chemical Engineering Division Summary Report, April–June 1963, USAEC Report ANL-6725, December 1963.
16. *Reactor Fuel Process.*, 5(4): 80 (October 1962).
17. R. G. Wymer and O. C. Dean, The Feasibility of Direct Gas-Phase Conversion of UF_6 to UC, USAEC Report ORNL-TM-669, Oak Ridge National Laboratory, Sept. 6, 1963.
18. L. M. Ferris, M. J. Bradley, and R. J. Gray, Phase Relationships in the Uranium-Carbon System as Determined by Chemical, Metallographic, and X-Ray Diffraction Methods, USAEC Report ORNL-TM-668, Oak Ridge National Laboratory, Sept. 3, 1963.
19. E. J. Huber, Jr., E. L. Head, and C. E. Holley, Jr., The Heat of Formation of Uranium Dicarbide, *J. Phys. Chem.*, 67(8): 1730-1731 (August 1963).
20. L. Jakesova and D. Jakes, Carbides, Nitrides, and Silicides of Uranium as Promising Nuclear Fuel, *At. Energy Rev.*, 1(3): 3-46 (1963).
21. T. Mukaibo and K. Naito, On the Thermochemical Properties of Uranium Carbides, *J. At. Energy Soc. Japan*, 5(7): 601-608 (July 1963) (in English).
22. P. E. Evans and T. J. Davies, Uranium Nitrides, *J. Nucl. Mater.*, 10(1): 43-55 (September 1963).
23. Implications of U-N Phase System for UN Fuel, *Nucleonics*, 22(1): 64 (January 1964).
24. R. D. Piper, Electrolytic Reduction of Uranium Oxides, in Process Development Quarterly Progress Report, January–March 1963, USAEC Report MCW-1480, Mallinckrodt Chemical Works, May 1, 1963.
25. *Reactor Fuel Process.*, 5(4): 82 (October 1962).
26. R. D. Piper, J. D. Vie, J. N. Reyland, R. J. Kornfeld, and D. E. Treadway, Methods for Tapping Molten Uranium from an Electrolytic Cell, USAEC Report MCW-1481, Mallinckrodt Chemical Works, Nov. 15, 1963.
27. D. G. Kesterke, L. W. Schramm, R. G. Knickerbocker, and T. A. Henrie, Electrowinning Uranium from Uranium Oxide, Report BM-RI-6226, Bureau of Mines, October 1962.
28. W. G. Smiley, Preparation of Uranium Metal by Carbon Reduction, USAEC Report NAA-SR-8507, Atomics International, 1962.
29. *Reactor Fuel Process.*, 5(1): 70 (January 1962).
30. Argonne National Laboratory, Chemical Engineering Division Summary Report, October–December 1962, USAEC Report ANL-6648, pp. 95-98, May 1963.
31. Argonne National Laboratory, Chemical Engineering Division Summary Report, January–March 1963, USAEC Report ANL-6687, pp. 60-62, 1963.
32. J. H. Cavendish, H. M. Beers, and M. A. DeSesa, Hydrometallurgical Processing of Uranium-Bearing Residue Materials to UF_4, USAEC Report NLCO-873, National Lead Co. of Ohio, November 1962; revised April 1963.
33. J. H. Mueller, W. P. Tolos, J. H. Cavendish, and T. J. Collopy, Uranous Chloride as a Reducing Agent for Iron in Scrap Recovery Plant Leach Liquor, in Summary Technical Report for the Period October 1, 1962, to December 31, 1962, USAEC Report NLCO-865, pp. 7-11, National Lead Co. of Ohio, Feb. 1, 1963.
34. N. R. Leist, Conversion of Low-Grade Uranium Residues to Winlo Feed, in Summary Technical Report for the Period January 1, 1963, to March 31, 1963, USAEC Report NLCO-870, pp. 7-32, National Lead Co. of Ohio, May 10, 1963.
35. C. W. Huntington, A. E. Abbott, M. G. Mendel, and D. R. Spadafora, Dehydration of Winlo Green Salt in HF, in Summary Technical Report for the Period July 1, 1963, to September 30, 1963, USAEC Report NLCO-890, pp. 39-44, Oct. 28, 1963.
36. Argonne National Laboratory, Chemical Engineering Division Summary Report, April–June 1962, USAEC Report ANL-6569, pp. 66-67, August 1962.
37. Argonne National Laboratory, Chemical Engineering Division Summary Report, July–September 1962, USAEC Report ANL-6596, pp. 91-93, 1963.
38. Argonne National Laboratory, Chemical Engineering Division Summary Report, October–December 1962, USAEC Report ANL-6648, pp. 90-95, May 1963.
39. Argonne National Laboratory, Chemical Engineering Division Summary Report, January–March 1963, USAEC Report ANL-6687, pp. 59-60, 1963.
40. Ames Laboratory, Annual Summary Research Report of Chemistry, Engineering, Metallurgy, Physics, and Reactor Divisions, July 1, 1962–June 30, 1963, USAEC Report IS-700, September 1963.

LEGAL NOTICE

This document was prepared under the sponsorship of the U. S. Atomic Energy Commission. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

NUCLEAR SCIENCE ABSTRACTS

The U. S. Atomic Energy Commission, Division of Technical Information, publishes *Nuclear Science Abstracts (NSA)*, a semimonthly journal containing abstracts of the literature of nuclear science and engineering.

NSA covers (1) research reports of the U. S. Atomic Energy Commission and its contractors; (2) research reports of government agencies, universities, and industrial research organizations on a world-wide basis; and (3) translations, patents, books, and articles appearing in technical and scientific journals.

Complete indexes covering subject, author, source, and report number are included in each issue. These are cumulated quarterly, semiannually, and annually providing a detailed and convenient key to the literature.

Availability of *NSA*

SALE *NSA* is available on subscription from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402, at $30.00 per year for the semimonthly abstract issues and $22.00 per year for the four cumulated-index issues. Subscriptions are postpaid within the United States, Canada, Mexico, and all Central and South American countries, except Argentina, Brazil, British and French Guiana, Surinam, and British Honduras. Subscribers in these Central and South American countries, and in all other countries throughout the world, should remit $37.00 per year for subscriptions to semimonthly abstract issues and $25.00 per year for the four cumulated-index issues.

EXCHANGE *NSA* is also available on an exchange basis to universities, research institutions, industrial firms, and publishers of scientific information. Inquiries should be directed to the Division of Technical Information Extension, U. S. Atomic Energy Commission, P. O. Box 62, Oak Ridge, Tennessee, 37831.

TECHNICAL PROGRESS REVIEWS may be purchased from Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402. *Isotopes and Radiation Technology* at $2.00 per year for each subscription or $0.55 per issue; the other four journals at $2.50 per year and $0.70 per issue. The use of the coupon below will facilitate the handling of your order.

POSTAGE AND REMITTANCE: Postpaid within the United States, Canada, Mexico, and all Central and South American countries except as hereinafter noted. Add $0.50 per year, or $0.15 per single issue for the *Isotopes and Radiation Technology* journal and $0.75 per year or $0.20 per single issue for the other four journals for postage to all other countries, including Argentina, Brazil, British and French Guiana, Surinam, and British Honduras. Payment should be by check, money order, or document coupons, and MUST accompany order. Remittances from foreign countries should be made by international money order, or draft on an American bank, payable to the Superintendent of Documents, or by UNESCO book coupons.

order form

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON , D. C., 20402

Enclosed:
document coupons ☐ check ☐ money order ☐

Charge to Superintendent of Documents No._____

Please send a one-year subscription to

☐ NUCLEAR SAFETY

☐ POWER REACTOR TECHNOLOGY

☐ REACTOR FUEL PROCESSING

☐ REACTOR MATERIALS

(Each subscription $2.50 per year; $0.70 per issue.)

☐ ISOTOPES AND RADIATION TECHNOLOGY

(Each subscription $2.00 a year; $0.55 per issue.)

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON, D. C., 20402

(Print clearly)

Name_____

Street_____

City_____ Zone____ State_____